# MODELLING OF NOVOLAC TYPE PHENOL-FORMALDEHYDE POLYMERIZATION

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By

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TO

MAA AND DEWTA

## CERTIFICATE

This is to certify that the work 'Modelling of Novolac Type Phenol Formaldehyde Polymerization' has been carried out under my supervision and has not been submitted elsewhere for a degree.

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## NOMENCLATURE

| | | |
|---|---|---|
| $M_n$ | = | Number average molecular weight |
| $M_w$ | = | Weight average molecular weight |
| $O_e, O_e'$ | = | Ortho external sites |
| $O_i$ | = | Ortho internal sites |
| $p_e$ | = | para external sites |
| $p_i$ | = | para internal sites |
| $P_i$ | = | Polymer molecule of chain length i with no ($-CH_2OH$) |
| $Q_i$ | = | Polymer molecule of chain length i with substituted $CH_2OH$ |
| r | = | rate of reaction |

Symbol

| | |
|---|---|
| [ ] | concentration |

## ABSTRACT

The kinetic model for irreversible novolac type for phenol formaldehyde polymerization is presented and equations governing the molecular weight distribution MWD of the polymer formed for both batch and homogeneous continuous flow stirred tank reactors (HCSTR) have been derived. The set of non-linear differential equations for batch reactor is solved using Runge-Kutta method of order 4 and the set of non-linear algebraic equations for HCSTRs is solved with the help of Brown's algorithm which is found to be more efficient than Newton's method. A sensitivity analysis of different reaction parameters have been carried out and the reactivity of the para position was found to be an important factor affecting the MWD. The results for HCSTR have also been compared with those for batch reactors and the former is found to give polymer of lower average molecular weights having higher polydispersity index. A model for the reversible case is also presented.

# CHAPTER 1

## Introduction:

There are several classes of condensation polymerization systems where Flory's equal reactivity hypothesis does not hold good[2]. Formation of Novolac type phenol formaldehyde polymer is one of the commercially important systems.

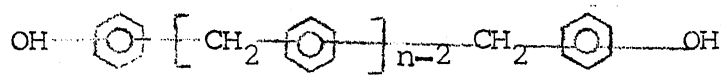
It is known that formaldehyde in water exists as methylene glycol ($OH - CH_2 - OH$) and therefore exhibits a functionality of two. Phenol on the other hand has three reactive sites, two ortho positions and one para positions and experimental studies have shown that they have different reactivities[2,3]. Also the studies on gelations have revealed that the polymer molecules grow mainly by the reactions of the end groups. Drum and LeBlanc have explained this phenomena through molecular shielding assigning lower reactivities to internal sites.

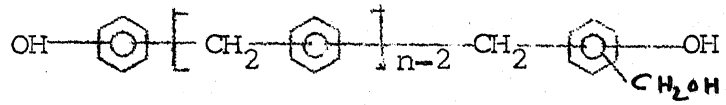
For polymerization systems where equal reactivity hypothesis holds, the expression for the reaction rate can be written in terms of reaction between functional groups. But in the case of novolac type polymerization one must write mass balance equations of individual polymer molecules of a given chain length in terms of reaction of these sites[1] and the resulting system of differential equations (including the balance equations of different sites) must be solved numerically for getting conversion and MWD.

# CHAPTER 2

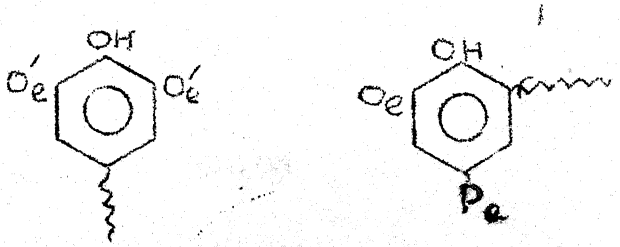
## Kinetic Model:

In the reaction mass, the polymer chains are assumed to consist of all those molecules which have chain lengths greater than 2. There are two kinds of molecular species

$P_n$ :  (a)

$Q_n$ :  (b) (1)

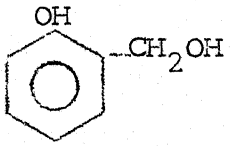
where the symbol  means that the bond formation has occured either at para or ortho position. The $P_n$ and $Q_n$ differ from each other only by substituted $-CH_2OH$. It is assumed that there is only one bound $CH_2OH$ per chain which can be anywhere on it. These molecules contain external ortho ($O_{eT}$) and para position ($p_e$) which are present at chain ends and internal ortho and para positions ($O_i$ and $p_i$) situated within the chain. All these positions have been shown to differ in their reactivities. The examination of chain ends reveals that the following two molecular structures can give rise to external ortho positions

 (2)

These are distinguished and denoted as $O_e'$ and $O_e$. The total number of external ortho positions $O_{eT}$, is the sum of these two.

At a given time in the reaction mass, there can be free formaldehyde molecules and bound $CH_2OH$ groups and the reactive sites can interact with both of these. The different reactions have been summarized in table 2.1. These reactions have been written to satisfy the site balance. As an example, reaction (a) table 2.1 stands for the fact that on reaction , $O_e'$, is assumed to be not available for further reaction which becomes $O_i$ on further reaction. This fact has been represented by writing--$O_e$ and + $O_i$ in the right hand side. The reactivity of these reactions is assumed to be completely determined by the reactive sites involved in them. In reactions (a) to (e) of the table, the rate constants have been multiplied by factor 2 because in the formaldehyde molecules, there are two (OH) groups where the reaction can occur with equal likelihood.

The schematic reactions shown in Table 2.1 do not include these involving phenol. When phenol reacts with formaldehyde, it forms the following two species:

$Q_1'$ :  and $Q_1$ :  (3)

Reactions of $Q_1$ and $Q_1'$ are also not covered by schematic equations of Table 2.1and they are all listed in Table 2.2. In reaction (a) of table 2.2 there are two positions on phenol (P) and two positions on F and therefore the reactivity has been shown to be $4k_1$ and so on. A mass balance on these species for batch reactors gives

$$\frac{d[O_e']}{dt} = -2k_1[O_e']\left[[Q_1] + 2[F] + [CH_2OH]\right] + [Q_1']\left[2k_1[O_e] + 2k_2[O_i] + 2k_3[P_i] + 2k_4[p_e] + 4(k_1+k_4)[P]\right] + \left[[Q_1] + [CH_2OH]\right] 2k_4 [P] \quad (4)$$

$$\frac{d[O_e]}{dt} = [Q_1]\left[k_1[O_e'] + k_2[O_i] + k_3[P_i] + (4k_1+k_4)[P]\right] - [Q_1'] \times \left[k_1[O_e] + k_4[p_e] - 2k_1[P]\right] - 2[F]\left[k_1[O_e] + k_4[p_e]\right] - [CH_2OH]\left[k_4[p_e] - 2k_1[P] + k_1[O_e]\right] \quad (5)$$

$$\frac{d[O_i]}{dt} = [Q_1]\left[k_1[O_e'] - k_2[O_i] + k_4[p_e]\right] + [Q_1']\left[k_1[O_e'] - k_2[O_i] + k_4[p_e]\right] + 2[F]\left[k_1[O_e'] - k_2[O_i] + k_4[p_e]\right] + [CH_2OH]\left[k_1[O_e'] - k_2[O_i] + k_4[p_e]\right] \quad (6)$$

$$\frac{d[P_i]}{dt} = k_1[O_e]\left[[Q_1] + [Q_1'] + 2[F] + [CH_2OH]\right] - k_3[P_i] \times \left[[Q_1] + [Q_1'] + 2[F] + [CH_2OH]\right] \quad (7)$$

$$\frac{d[P_e]}{dt} = [Q_1]\left[k_1[O_e'] + k_2[O_i] + (4k_1+k_4)[P] + k_3[P_i]\right] + [Q_1'] \times \left[2k_1[P] - k_1[O_e] - k_4[P_e]\right] - 2[F]\left[k_1[O_e] + k_4[P_e]\right] + [CH_2OH]\left[2k_1[P] - k_4[P_e]\right] \quad (8)$$

$$\frac{d[Q_1]}{dt} = 4k_1[F][P] - 2(k_1+k_4)[Q_1][P] - [Q_1]\left[k_1[O_e'] + k_1[O_e] + k_2[O_i] + k_3[P_i] + k_4[P_e]\right] - 2(k_1+k_4)[Q_1]^2 - (3k_1+k_4) \times [Q_1][Q_1'] - (k_1+k_4)[Q_1][CH_2OH] \quad (9)$$

$$\frac{d[Q_1']}{dt} = 2k_4[P][F] - (2k_1+k_4)[Q_1'][P] - [Q_1']\left[k_1[O_e'] + k_1[O_e] + k_2[O_i] + k_3[P_i] + k_4[P_e]\right] - 4k_1[Q_1']^2 - (3k_1+k_4)[Q_1] \times [Q_1'] - 2k_1[Q_1'][CH_2OH] \quad (10)$$

$$\frac{d[F]}{dt} = -2[F]\left[(2k_1+k_4)[P] + k_1[O_e'] + k_1[O_e] + k_2[O_i] + k_3[P_i] + k_4[P_e]\right] \quad (11)$$

$$\frac{d[P]}{dt} = -(2k_1+k_4)[P]\left[[Q_1] + [Q_1'] + 2[F] + [CH_2OH]\right] \quad (12)$$

Modelling of Molecular Weight Distribution:

In previous studies[1] it has shown that the concentration of bound $CH_2OH$ in the reaction mass is small. In view of this, it is assumed that a polymer molecule in the reaction mass either has one bound $CH_2OH$ or has none. In view of this, the growth of polymer molecules can be represented by following reactions:

$$P_n + F \longrightarrow Q_n \qquad (a)$$

$$Q_n + P_m \longrightarrow P_{n+m} \quad n,m = 2,3 \ldots \qquad (b) \qquad (13)$$

and

$$Q_n + Q_m \longrightarrow Q_{n+m} \quad n,m = 2,3 \ldots \qquad (c)$$

The reaction between $Q_n$ and $Q_m$ can occur in two ways:

(a) reactive sites on $Q_n$ react with $(-CH_2OH)$ on $Q_m$

and (b) reactive sites on $Q_m$ react with $(-CH_2OH)$ on $Q_n$

If $o_eQ_n$, $o'_eQ_n$ $o_iQ_n$, $p_iQ_n$ and $p_eQ_n$ are total number of sites on all $Q_n$ in the reaction mass and $o_eQ_m$, $o'_eQ_m$, $o_iQ_m$, $p_iQ_m$, and $p_eQ_m$ on all $Q_m$ in the system, the reaction rate, $r_{mn}$ between $Q_n$ and $Q_m$ can be written as

$$r_{mn} = (k_1 o_e Q_n + k_1 o'_e Q_n + k_2 o_i Q_n + k_3 p_i Q_n + k_4 p_e Q_n)[Q_m]$$

$$+(k_1 o_e Q_m + k_1 o'_e Q_m + k_2 o_i Q_m + k_3 p_i Q_m + k_4 p_e Q_m)[Q_n]$$

$$m,n = 3,4 \qquad (14)$$

The above equation must be modified when either m or n is equal to 2

This is because polymer molecules of chain length 2 do not have internal sites and the above equation is modified to

$$r_{m2} = (k_1\, o_e\, Q_m + k_1 o'_e\, Q_m + k_2\, o_i Q_m + k_3 p_i Q_m + k_4 p_e\, Q_m)\ [Q_2]$$

$$+ (k_1\, o_e Q_2 + k_1 o'_e\, Q_2 + k_4 p_e\, Q_2)\ [Q_m] \quad m = 3,4 \qquad (15)$$

The reaction between $Q_n$ and $P_m$, however, would not obey equations (13) and (14) because the bound $CH_2OH$ of $Q_n$ alone can react with reactive sites of $P_m$. Thus, the corresponding rate of reaction, $r'_{mn}$, can be written as

$$r'_{mn} = (k_1\, o_e P_m + k_1 o'_e\, P_m + k_2 o_i\, P_m + k_3\, p_i\, P_m$$

$$+ k_4 p_e\, P_m)\ [Q_n] \quad n = 2,3 \ldots\ldots$$

$$m = 3,4 \qquad (16)$$

When m = 2, the above equation must be modified to

$$r_{2n} = (k_1\, o_e\, P_2 + k_1\, o'_e\, P_2 + k_4 p_e\, P_2)\ [Q_n] \quad n = 2,3 \ldots \qquad (17)$$

To find $o_e\, Q_n$, it is noted that

$$o_e Q_n = [Q_n]\ (\text{Average fraction of sites on } Q_n \text{ that are } o_e) \qquad (18)$$

The fraction of sites on $Q_n$ is assumed to be the same, on an average, as that of the overall average in the reaction mass. In other words,

$$o_e\, Q_n \simeq [Q_n]\ (\text{overall fraction of } o_e \text{ sites on all}$$

polymer molecules)

$$= [Q_n] \left\{ \frac{[O_e]}{\sum_2 [P_n] + \sum_2 [Q_n]} \right\} \qquad (19)$$

Following relations are written for other reactive sites as

$$O'_e\, Q_n = \frac{[O'_e]\,[Q_n]}{SUM} \qquad (a)$$

$$O_i Q_n = \frac{[O_i]\,[Q_n]}{SUM} \qquad (b)$$

$$P_i\, Q_n = \frac{[P_i]\,[Q_n]}{SUM} \qquad (c)$$

$$P_e\, Q_n = \frac{[P_e]\,[Q_n]}{SUM} \qquad (d) \qquad (20)$$

where

$$SUM = \left( \sum_2 P_n + \sum_2 Q_n \right) \qquad (21)$$

Similar relations are valid and can be written for $O_e P_n$, $O'_e P_n$ etc. In terms of these, equations (14) to (17) can be easily written as

$$r_{mn} = \frac{2\,CN}{SUM} [Q_m]\,[Q_n] \qquad (a)$$

$$r_{m2} = \frac{CN}{SUM} [Q_m]\,[Q_2] + \frac{CM}{SUM} [Q_m][Q_2] \qquad (b)$$

q $$r'_{mn} = \frac{CN}{SUM} [P_m][Q_n] \quad (c)$$

$$r'_{2n} = \frac{CM}{SUM} [P_2][Q_m] \quad (d) \qquad (22)$$

where

$$CN = k_1[O_e] + k_1[O'_e] + k_2[O_i] + k_3[P_i] + k_4[P_e] \quad (a)$$

and $$CM = k_1[O_e] + k_1[O'_e] + k_4[P_e] \quad (b) \qquad (23)$$

Now one is in position to carry out the mass balance on $P_n$ and $Q_n$ which is done as follows. For the mass balance of $Q_n$ it is noted that it is formed when $P_n$ reacts with formaldehyde and $Q_m$ reacts with $Q_{n-m}$ where m could have any value between 1 and (n-1). $Q_n$ is destroyed when it reacts with phenol or $P_n$ and $Q_m$ where m =2,3...., The balance for a batch reactor yields

$$\frac{d[Q_n]}{} = -(2k_1+k_4)[P][Q_n] - \left\{CN[Q_n] + \frac{CN}{SUM}[Q_n]\left(\sum'_{m=2}[Q_m] + [Q_1] + [Q'_1]\right) + (2k_1[Q'_1] + k_1[Q_1] + k_4[Q_i])[Q_n]\right\} + \frac{2\,CN}{SUM}[F][P_n]$$

$$+ \frac{CN}{SUM}\sum_{i=2}^{n-3}[Q_i][Q_{n-i}] + \frac{CM}{SUM}[Q_2][Q_{n-2}] + \frac{CN}{SUM}$$

$$[Q_1][Q_{n-1}] + (k_1+k_4)[Q_1][Q_{n-1}] + \frac{CN}{SUM}[Q_{n-1}][Q'_1]$$

$$+ 2k_1[Q'_1][Q_{n-1}] \quad n \geq 4 \qquad (24)$$

The relation above is valid for $n \geq 4$ and the balances for $Q_2$ and $Q_3$ are

$$\frac{d[Q_2]}{dt} = (k_1+k_4)[Q_1]^2 + 3(k_1+k_4)[Q_1][Q_1'] + 2k_1[Q_1']^2 + \frac{2\,CM}{SUM}[P_2][F]$$
$$-(2k_1+k_4)\left([Q_2][P] - CN[Q_2] - \frac{CM}{SUM}[Q_2]\left(\sum_2[Q_m] + [Q_1] + [Q_1']\right)\right)$$
$$-[Q_2]\,(2k_1[Q_1'] + k_1[Q_1] + k_4[Q_1]) \qquad (25)$$

and

$$\frac{d[Q_3]}{dt} = -(2k_1+k_4)[Q_3][P] - CN[Q_3] - \frac{CN}{SUM}[Q_3]\left(\sum_2[Q_m] + [Q_1] + [Q_1']\right) + \frac{2\,CN}{SUM}[P_3][F] + (k_1+k_4)[Q_1][Q_2] + 2k_1[Q_1'][Q_2]$$
$$+\frac{CM}{SUM}[Q_2]\,([Q_1] + [Q_1']) - (2k_1[Q_1'] + k_1[Q_1] + k_4[Q_1])[Q_3] \qquad (26)$$

On summation of equations (24) to (26), one obtains

$$\frac{d[-CH_2OH]}{dt} = \frac{d\sum_2^{\infty}[Q_n]}{dt} = -(2k_1+k_4)[P]\sum_{n=2}^{\infty}[Q_n] - CN\sum_{n=2}^{\infty}Q_n$$
$$+\frac{2[F]}{SUM}\left(CN\sum_{n=3}^{\infty}[P_n] + CM[(P_2)\right) + (k_1+k_4)[Q_1]^2$$
$$+(3k_1+k_4)[Q_1][Q_1'] + 2k_1[Q_1]^2 \qquad (27)$$

A smilar mass balance can be made on $P_n$. It is noted that $P_n$ is formed when $P_{n-1}$ reacts with $Q_1$ or $Q_1'$ and $P_{n-i}$ reacts w..h

$Q_i$. It is destroyed when it reacts with formaldehyde and any $Q_m$. The balance gives

$$\frac{d[P_n]}{dt} = \frac{CN}{SUM}[P_{n-1}]\left([Q_1] + [Q_1']\right) + \sum_{i=2}^{n-3} \frac{CN}{SUM}[P_{n-i}][Q_i]$$

$$+ \frac{CM}{SUM}[P_2][Q_{n-2}] + (2k_1+k_4)[P][Q_{n-1}] - \frac{2\,CN}{SUM}[P_n][F]$$

$$- \frac{CN}{SUM}[P_n]\left(\sum_2 [Q_m] + [Q_1] + [Q_1']\right) \qquad n \geq 5 \qquad (28)$$

The above equation is valid only for $n \geq 5$ and therefore balances for $P_2$, $P_3$ and $P_4$ are written as

$$\frac{d[P_2]}{dt} = (2k_1+k_4)[P]\left([Q_1] + [Q_1']\right) - \frac{2\,CM}{SUM}[P_2][F]$$

$$- \frac{CM}{SUM}[P_2]\left(\sum_2 [Q_m] + [Q_1] + [Q_1']\right) \qquad (29)$$

$$\frac{d[P_3]}{dt} = \frac{CM}{SUM}[P_2]\left([Q_1] + [Q_1']\right) + (2k_1+k_4)[P][Q_2] - \frac{2CN}{SUM}[P_3][F]$$

$$- \frac{CN}{SUM}[P_3]\left(\sum_2 [Q_m] + [Q_1] + [Q_1']\right) \qquad (30)$$

$$\frac{d[P_4]}{dt} = \frac{CN}{SUM}[P_3]\left([Q_1] + [Q_1']\right) + \frac{CM}{SUM}[P_2][Q_2] + (2k_1+k_4)[P]$$

$$\times [Q_3] - \frac{2CN}{SUM}[P_4][F] - \frac{CN}{SUM}[P_4]\left(\sum_2 [Q_m] + [Q_1] + [Q_1']\right)$$

(31)

To calculate the molecular weight distribution, eqns. (4) to (12) and (27) must be solved simultaneously and substituted in eqns. (24) to (28), to obtain $[P_n]$ and $[Q_n]$ as a function of time. These equations are written in dimensionless form using following variables.

$$y_1 = \frac{[O_e']}{[F]_o} \qquad (a)$$

$$y_2 = \frac{[O_e]}{[F]_o} \qquad (b)$$

$$y_3 = [O_i] / [F]_o \qquad (c)$$

$$y_4 = [P_i] / [F]_o \qquad (d)$$

$$y_5 = [P_e] / [F]_o \qquad (e)$$

$$y_6 = [Q_1] / [F]_o \qquad (f)$$

$$y_7 = [Q_1'] / [F]_o \qquad (g)$$

$$y_8 = [F] / [F]_o \qquad (h)$$

$$y_9 = [P] / [F]_o \qquad (i)$$

$$y_{10} = [CH_2OH] / [F]_o \qquad (j)$$

$$y_{11} = [P_2] / [F]_o \qquad (k)$$

$$x = k_1 [F]_o t \qquad (l)$$

$$y_{P_i} = [P_i] / [F]_o \quad i = 3,4 \qquad (m)$$

$$Y_{Q_i} = [Q_i] / [F]_o \quad i = 2,3..... \qquad (n)$$

$$R_1 = (k_2/k_1) \qquad (o)$$

$$R_2 = (k_3/k_1) \qquad (p)$$

$$R_3 = (k_4/k_1) \qquad (q)$$

Homogeneous Continous Flow Stirred Tank Reactor[4]

The rate equations derived for batch reactor can be incorporated in the steady state HCSTR simulation as follows:

Rate of input + Rate of generation due to reaction

= Rate of out put

For $P_n$ and $Q_n$

$$v [P_n]_o + V (r_{P_n}) = v [P_n]$$

or

$$[P_n]_o - [P_n] + \tau \frac{d[P_n]}{dt} = 0$$

$$[Q_n]_o - [Q_n] + \tau \frac{d[Q_n]}{dt} = 0$$

where $r_{P_n}$ = rate of formation of $P_n$

v = volume flow rate volume/time

V = volume of reactor volume

$[Q_n]_o$, $[P_n]_o$ = input concentration mole/volume

$[Q_n]$, $[P_n]$ = out put concentration mole/ volume

$\tau$ = residence time

Similar equations can be written for all the sites, P , F

$Q_1$ , $Q_1'$ and $Q_n$ . Thus we get a system of nonlinear algebraic equations. Since equation for $-CH_2OH$ is a dependent one, it is not incorporated. We get $-CH_2OH$ from the relation

$$[-CH_2OH] = \sum_{n=2}^{\infty} [P_n] + [Q_n]$$

The mole fraction distribution $MFDP_i$ and $MFDQ_i$ of species $P_i$ and $Q_i$ resepctively have been defined as

$$MFDP_i + = \frac{[P_i]}{\sum_{i=2}^{\infty} [P_i] + [P]} \qquad i=1,2,\ldots$$

$$MFDQ_i = \frac{[Q_i]}{\sum_{i=1}^{\infty} [Q_i] + [Q_1']} \qquad i=1,2,\ldots$$

In the above equation for n=1 in $MFDQ_i$, $Q_{1T}$ is equal to ( $Q_1$ + $Q_1'$ ) has been used in the calculation.

In the weight fraction distributions, $WFDP_i$ and $WFDQ_i$, as opposed to this, the total weight of the reaction mass at the time of interest has been made as the basis as follows:

$$WFDP_i = \frac{WP_i}{\sum_{i=2}^{\infty} WP_i + \sum_{i=1}^{\infty} WQ_i + WP + WQ_1'}$$

and

$$WFDQ_i = \frac{WQ_i}{\sum_{i=2}^{\infty} WP_i + \sum_{i=1}^{\infty} WQ_i + WP + WQ_1'}$$

where $WP_i$, $WQ_i$, WP and $WQ_1'$ refer to the weight of species $P_i$, $Q_i$, P and $Q_1'$ respectively.

TABLE 2.1

Reactions of $O_e$, $O_e'$, $P_i$, $O_i$ and $P_e$

(1) With formaldehyde

$$O_e' + F \xrightarrow{2k_1} (-CH_2OH) + O_i - O_e' \quad (a)$$

$$O_e + F \xrightarrow{2k_1} (-CH_2OH) + P_i - P_e \quad (b)$$

$$O_i + F \xrightarrow{2k_2} (-CH_2OH) \quad (c)$$

$$P_i + F \xrightarrow{2k_3} (-CH_2OH) \quad (d)$$

$$P_e + F \xrightarrow{2k_4} (-CH_2OH) + O_i - O_e \quad (e)$$

(2) With bound formaldehyde ($-CH_2OH$)

$$O_e' + (-CH_2OH) \xrightarrow{k_1} O_i - O_e' \quad (f)$$

$$O_e + (-CH_2OH) \xrightarrow{k_1} P_i - P_e \quad (g)$$

$$O_i + (-CH_2OH) \xrightarrow{k_2} \text{consumption} \quad (h)$$

$$P_i + (-CH_2OH) \xrightarrow{k_3} \text{consumption} \quad (i)$$

$$P_e + (-CH_2OH) \xrightarrow{k_4} O_i - O_e \quad (j)$$

TABLE 2.2

Reactions of P, $Q_1$ and $Q_1'$

(a) Reactions of P with F and $(-CH_2OH)$

$$P+F \xrightarrow{4k_1} Q_1 \quad (a)$$

$$P+F \xrightarrow{2k_4} Q_1' \quad (b)$$

$$P+(-CH_2OH) \xrightarrow{2k_1} p_e + o_e \quad (c)$$

$$P+(-CH_2OH) \xrightarrow{k_4} 2\,o_e' \quad (d)$$

(b) Reactions of P with $Q_1$ and $Q_1'$

$$P + Q_1' \xrightarrow{2k_1} p_e + 2o_e' + o_e \quad (e)$$

$$P + Q_1' \xrightarrow{k_4} 4\,o_e' \quad (f)$$

$$P + Q_1 \xrightarrow{2k_1} 2p_e + 2o_e \quad (g)$$

$$P + Q_1 \xrightarrow{k_4} o_e + P_e + 2o_e' \quad (h)$$

(c) Reactions of $Q_1$ and $Q_1'$ with reactive sites

$$o_e' + Q_e' \xrightarrow{k_1} o_i + 2o_e' - o_e' \quad (i)$$

$$o_e' + Q_1 \xrightarrow{k_1} p_e + o_e + o_i - o_e' \quad (j)$$

$$o_e + Q_1 \xrightarrow{k_1} p_e + o_e + p_i - p_e \quad (k)$$

$$o_e + Q_1' \xrightarrow{k_1} 2o_e' + p_i - p_e \quad (l)$$

$$p_i + Q_1 \xrightarrow{k_3} o_e + p_e \qquad (m)$$

$$p_i + Q_1' \xrightarrow{k_3} 2o_e' \qquad (n)$$

$$o_i + Q_1' \xrightarrow{k_2} 2o_e' \qquad (q)$$

$$o_i + Q_1 \xrightarrow{k_2} o_e + p_e \qquad (r)$$

$$p_e + Q_1 \xrightarrow{k_4} o_i + o_e + p_e - o_e \qquad (s)$$

$$p_e + Q_1' \xrightarrow{k_4} o_i + 2o_e' - o_e$$

# CHAPTER 3

## NUMERICAL SOLUTIONS

### 1. Runge Kutta Method of Order 4:

The system of nonlinear differential equations for the batch reactor are solved in DEC 1090 computer using Runge Kutta Method of order 4. After a few trial, the stable solution was found for $x = 10^{-3}$. The algorithm of the technique is as follows[6]:

For the equation

$$y_1' = f_1 (x_1, x_2, x_3, \ldots\ldots, x_n)$$

$$y_2' = f_2 (x_1, x_2, x_3, \ldots\ldots, x_n)$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$y_n' = f_n (x_1, x_2, x_3, \ldots\ldots, x_n)$$

with $\bar{y}\ (\bar{x}_0) = \bar{y}_0$ where the bar indicates array gnerate approximations $\bar{y}_n$ to $\bar{y}\ (\bar{x}_0 + n \Delta x)$ for $\Delta x$ fixed and for n $n=0,1,2,\ldots$ using recursion formula

$$\bar{y}_{n+1} = \bar{y}_n + \frac{1}{6} (k_1 + 2k_2 + 2k_3 + k_4)$$

where

$$k_1 = x\ f\ (\bar{x}_n)$$

$$k_2 = x\ f\ (\bar{x}_n + \frac{\Delta x}{2})$$

$$k_3 = x\ f\ (\bar{x}_m + \frac{\Delta x}{2})$$

$$k_4 = x\ f\ (\bar{x}_n + \Delta x)$$

2. Brown's Method[5]:

The following system of nonlinear algebraic equations is considered

$$\begin{aligned} f_1(\bar{x}) &= f_1(x_1, x_2, \ldots, x_N) = 0 \\ f_2(\bar{x}) &= f_2(x_1, x_2, \ldots, x_N) = 0 \\ &\cdots \\ f_N(\bar{x}) &= f_N(x_1, x_2, \ldots, x_N) = 0 \end{aligned} \tag{3.1}$$

which can be written in vector form as $\bar{f}(\bar{x}) = \bar{0}$.

It is assumed that $f_i$ are continuously differentiable. In Newton Raphson technique the functions in equations 3.1 are expanded about a point $\bar{x}^n$ which is close to the solution $\bar{x}^*$ yielding

$$\bar{f}(\bar{x}) = \bar{f}(\bar{x}^n) + J(\bar{x}^n) \cdot (\bar{x} - \bar{x}^n) + \text{H.O.T.} \tag{3.2}$$

where the higher order terms (H.O.T.) are negligible and only the first order terms are included. Since $\bar{x}^n$ are close to $\bar{x}^*$ one therefore has

$$\bar{f}(\bar{x}) = \bar{0} \quad \text{or} \quad \bar{0} - \bar{f}(\bar{x}^n) + J(\bar{x}^n) \cdot (\bar{x} - \bar{x}^n)$$

Solving for $\bar{x}$ gives

$$\bar{x}^{n+1} = \bar{x} = \bar{x}^n - J^{-1}(\bar{x}^n) \cdot \bar{f}(\bar{x}^n) \tag{3.3}$$

The solution procedure would therefore be the following:

Begining with a starting guess, $\bar{x}^0$ one solves equations 3.3 iteratively for n= 0,1,2,.... This can be done only when $J(\bar{x})$

is non-singular in a suitable neighbourhood of $\bar{x}^*$. A derivative free analogue of Newton's method often called the discrete Newton's method is obtained from equation 3.3 by replacing the ith row and jth column entry of the Jacobian matrix (i.e. $\frac{\partial f_i}{\partial x_j}$) by the first difference quotient approximation

$$\frac{f_i(\bar{x}^n + h^n \bar{e}_j) - f_i(\bar{x}^n)}{h^n} \qquad (3.4)$$

Here $\bar{e}_j$ denotes the jth unit factor and scalar $h^n$ is normally chosen such that $h^n = 0$ (ll f ($\bar{x}^n$) ll ).

Brown technique calls the functions of equation 3.1 one at a time so that information obtained from working with $f_1$ can be incorporated in while working with $f_2$, etc. A successive substitution scheme is used rather than the simultaneous treatment of the $f_i$, as done in Newton's method. The former method is derivative free and its second order convergence has been proved. The method consists of applying the following steps:

Step 1:

Let $\bar{x}^n$ denote an approximation to the solution $\bar{x}^*$ of 3.1. The first function $f_1$ is expanded in an approximate Taylor series expansion about the point $\bar{x}^n$. By approximate it is meant the expansion in which the actual (analytic) partial derivatives are replaced by first difference quotient approximation.

$$f_1(\bar{x}) = f_1(\bar{x}^n) + f_{1x_1;h}(\bar{x}^n) \cdot (x_1 - x_1^n) + f_{1x_2;h}(\bar{x}^n) \cdot$$

$$(x_2 - x_2^n) + \ldots\ldots + f_{1x_n;h}(\bar{x}^n) \cdot (x_N - x_N^n) \qquad (3.5)$$

Here $f_{1x_j;h}(\bar{x}^n)$ is defined to be the first difference quotient approximation 3.4 with i=1. If $\bar{x}^n$ is close enough to $\bar{x}^*$, $f_1(\bar{x}) \simeq 0$ and equation 3.5 is equated to zero and solved for that variable, say $x_N$, whose corresponding approximate partial derivative, $f_{1x_N;h}(\bar{x}^n)$ is the largest in absolute value. This gives

$$x_N = x_N^n - (f^n_{1x_j;h}/f^n_{1x_N;h}) \cdot (x_j - x_j^n) - f_1^n/f^n_{1x_N;h} \qquad (3.6)$$

where $f_{1x_j;h} = f_{1x_j;h}(\bar{x}^n)$ as given in 3.4 and $f_1^n = f_1(\bar{x}^n)$. The constants $f^n_{1x_j;h}/f^n_{1x_N;h}$ are saved (stored) in the computer implementation of the algorithm for future use. By choosing the approximate partial derivatives of the largest value to divide by a partial pivoting effect is achieved, similar to what is often done when using the Gaussian elimination process for solving linear systems. This enhances the numerical stability of the method. It is observed from equation 3.6 that $x_N$ is a linear function of the N-1 variables $x_1, x_2, \ldots, x_{N-1}$ and for the purpose of clarity, the left hand side of 3.6 is redefined as

$L_N(x_1, x_2, \ldots, x_{N-1})$ and define $L_N^n = L_N(x_1^n, x_2^n, \ldots, x_{N-1}^n)$

Step 2:

Now a new function $g_2$ of N-1 variables $x_1,\ldots,x_{N-1}$ is redefined which is related to the second function $f_2$ of equation 3.1 as

$$g_2(x_1,\ldots,x_{N-1}) = f_2\ (x_1,\ldots,x_{N-1},\ L_N(x_1,\ldots,x_{N-1})) \quad (3.7)$$

Let $g_2^n$ be defined as $g_2^n = f_2\ (x_1^n,\ldots,x_{N-1}^n,\ L_N^n)$. Now $g_2$ is expanded in an approximate Taylor series expansion about the point $(x_1^n,\ \ldots x_{N-1}^n)$, linearized (ignoring higher order terms) and solved for that variable, say $x_{N-1}$, whose corresponding approximate partial derivative $g_{2x_{N-1};h}$ is largest in mangnitude,

$$x_{N-1} = x_{N-1}^n - \sum_{j=1}^{N-2} (g_2^n\ x_j;h / g_{2x_{N-1};h}^n)\cdot (x_j - x_j^n) - g_2^n / g_{2x_{N-1};h}^n \quad (3.8)$$

Here the approximate partial derivative $g_{2x_j;h}^n$ is given by

$$g_{2x_j;h}^n = \frac{g_2(x_1^n,\ldots,x_{j-1}^n,x_j^n + h^n,x_{j+1}^n,\ldots,x_{N-1}^n) - g_2^n}{h^n} \quad (3.9)$$

where $h^n$ is a small positive number. From equation 3.8 it is noted that $x_{N-1}$ is a linear function of the remaining N-2 variables and it is denoted by $L_{N-1}(x_1,\ldots,x_{N-2})$. Again the ratios $g_{2x_j;h}^n / g_{2x_{N-1};h}^n$, $j=1,\ldots,N-2$ and $g_2^n / g_{2x_{N-1};h}^n$ are stored for future use.

Step 3:

One defines

$$g_3(x_1,\ldots,x_{N-2}) = f_3(x_1,\ldots x_{N-2}, L_{N-1}, L_N) \qquad (3.10)$$

with the argument of $L_{N-1}$ being $(x_1,\ldots,x_{N-2})$ and the argument of $L_N$ being

$$x_1, x_2,\ldots,x_{N-2}, L_{N-1}(x_1,x_2,\ldots,x_{N-2}) \qquad (3.11)$$

One carries out 1) approximate Taylor expansion of the function $g_3$ about $(x_1^n,\ldots x_{N-2}^n)$ followed by 2) linearization of the resulting expansion followed by 3) equating to zero and solving for one variable, say $x_{N-2}$ (whose corresponding approximate partial derivative $g_{3x_{N-2};h}$ is largest in magnitude) as a linear combination $L_{N-2}$, of the now remaing N-3 variables. It is continued in this fashion, eliminating one variable for each equation treated. Every time a new linear expression, $L_{N-k}$, for one of the variables, say $x_{N-k}$, is obtained in terms of the remaining N-k-1 variables, $x_1,x_2,\ldots x_{N-k-2},x_{N-k-1}$. This linear expression is used whereever $x_{N-k}$ had appeared in the previously defined linear expressions $L_{N-k+1}, L_{N-k+2},\ldots L_N$. It may be noted that each step in the alogrithm adds one more linear expression to a linear system. During the k+1 st step of algorithm, it is necessary to evaluate $g_{k+1}$ i.e. $f_{k+1}$, for various arguments. The values of the last k components of the argument of $f_{k+1}$ are obtained by back substitution in the linear system $L_N, L_{N-1},\ldots L_{N-k+1}$

which has already been found. The points which are back substituted consist of the point $(x_1^n,\ldots,x_{N-k}^n) = \bar{x}_{N-k}^n$ together with the points $x_{N-k}^n + h^n\bar{e}_j$, $j=1,\ldots,N-k$, where $\bar{e}_j$ denoted the jth unit vector. The arguments are required to determine the quantitities $g_{k+1}^n$ and $g_{k+1,j;h}^n$, $j=1,\ldots,N-k$, needed for the elimination of the k+1 st variable; say $x_{N-k}$, by the basic processes of expansion, linearization and solution of the resulting expression. This process results for each k, in the k+1 st variable, say $x_{N-k}$, being expressed as linear combination $L_{N-k}$ of the remaining N-k-1 variables.

Step N:

In the last step

$g_N = f_N(x_1, L_2, L_3\ldots, L_N)$ where $L_j$'s are obtained by back substitution in the N-1 rowed triangular linear system which now has the form

$$L_i = x_i^n - \sum_{j=1}^{i-1} \left(g_{N-i+1,x_j;h}^n / g_{N-i+1,x_i;h}^n \cdot (L_j - x_j^n) - g_{N-1+1}^n / g_{N-i+1,x_i;h}^n\right), \quad i=N,N-1,\ldots 2 \qquad (3.12)$$

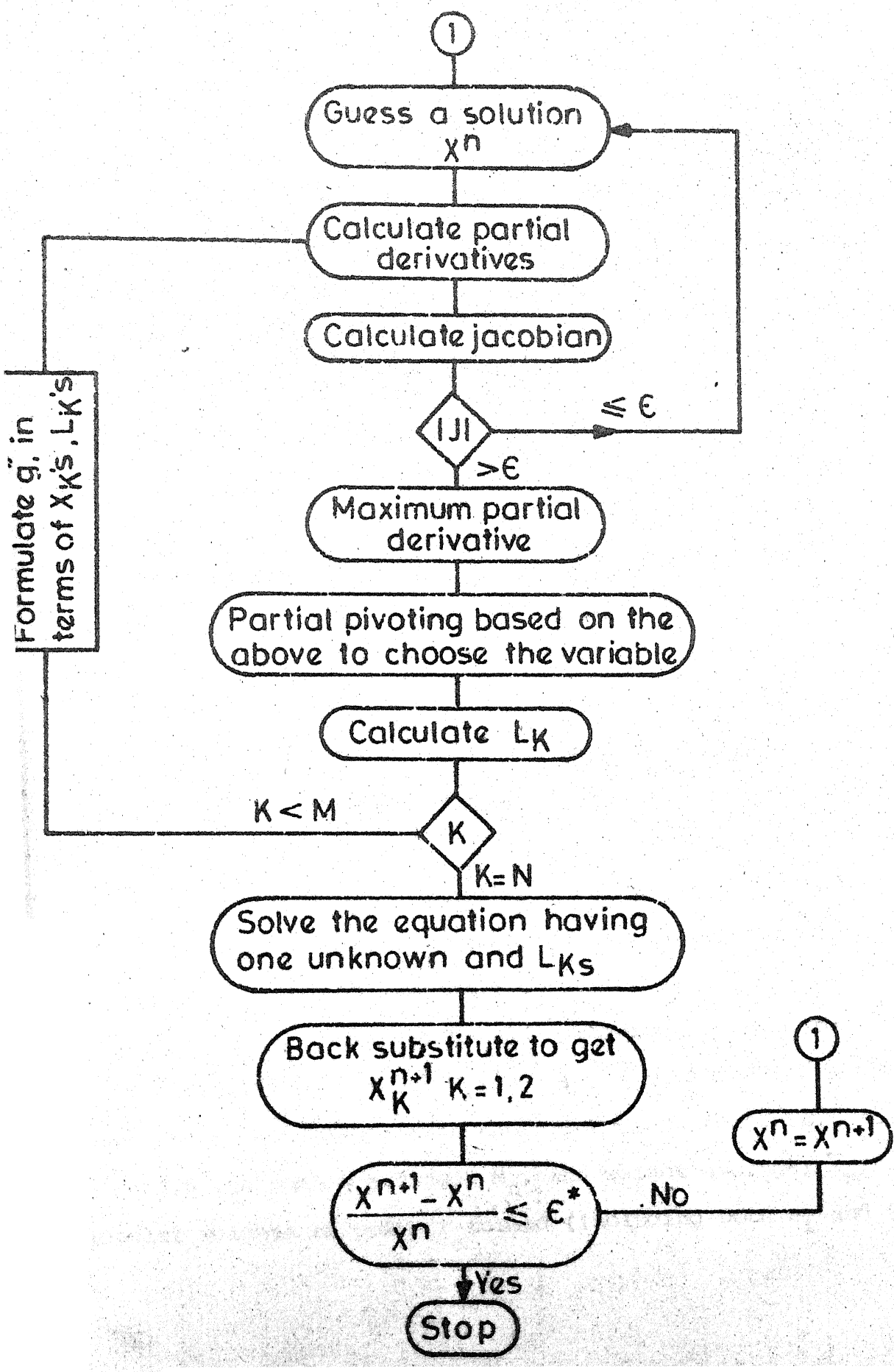
with $g_1 = f_1$ and $L_1 = x_1$) so that $g_N$ is just a function of the single variable $x_1$. Now expanding, linearizing and solving for $L_1$, one obtains

$$x_1 = x_1^n - g_N^n / g_{N,x_1;h}^n$$

This point $x_1$ thus obtained is used as the next approximation,

$x_1^{n+1}$, two the first component $x_1^*$, of the solution vector $\bar{x}^*$. $x_1$ is renamed as $L_1$ and the $L_j$ system in equation 3.12 is solved to get improved approximations of other components of $\bar{x}^*$.

The successive substitution nature of the algorithm allows the most recent information available to be used in the construction of the next function argument similar to what is done in the Gauss-Seidel process for linear and nonlinear systems of equations. A, simplified flow chart of the Brown's method is shown in figure 3.1


1
Guess a solution $X^n$
Calculate partial derivatives
Calculate jacobian
|J|
$\leq \epsilon$
$>\epsilon$
Maximum partial derivative
Partial pivoting based on the above to choose the variable
Calculate $L_K$
K
$K < M$
$K = N$
Formulate $\tilde{q}_i$ in terms of $X_K$'s, $L_K$'s
Solve the equation having one unknown and $L_K$s
Back substitute to get $X_K^{n+1}$ $K = 1, 2$
$\frac{X^{n+1} - X^n}{X^n} \leq \epsilon^*$
No
Yes
$X^n = X^{n+1}$
1
Stop

# CHAPTER 4

## RESULTS AND DISCUSSION

The mass balance equations for both batch as well as HCSTR are solved numerically in a DEC-1090 computer to examine the effects of various system parameters on molecular weights and conversions.

In figure 4.1 and 4.2 the mole fraction distributions (MFD) of $P_i$ and $Q_i$ have been plotted for different residence times of polymerization in HCSTR. On the same graph, the corresponding results for batch reactors have been given for comparison. As the time of polymerization increases, the distributions are found to become broader. For any given $\bar{x}$, the conversion of phenol is always lower and $[Q_{1T}]$ $(= [Q_1] + [Q_1']$ is higher for the HCSTR. In view of lower conversion of phenol, the concentration of higher homologs are naturally lower than those obtained in batch reactors. In figure 4.3 and 4.4, the corresponding weight fraction distributions (MWD) for HCSTRs as well as batch reactors are given. The distribution for batch reactors in figure 4.3 undergoes a maximum at n=2 for residence times beyond x=0.3, whereas no such behaviour is seen for HCSTRs. The distribution curves for $P_i$ as well as $Q_i$ for HCSTR's are always found to be lower than those for batch reactors. In figure 4.5 the number average, $\bar{M}_n$, and weight average, $\bar{M}_w$, molecular weights of polymer formed (including both $P_i$ and $Q_i$)

in the reaction mass for batch as well as HCSTRs has been plotted as a function of time. As expected, $\bar{M}_n$ and $\bar{M}_w$ for the latter are always found to be lower; however the polydispersity index, $\int$, for HCSTR is larger.

In figure 4.6 and 4.7, the effect of $R_3$ on the mole fraction distribution of $P_i$ and $Q_i$ at dimensionless residence time x=0.9 has been examined. In figure 4.6 for a given $R_3$, the distribution of $P_i$ falls monotonically and beyond n=10, it is almost zero and as $R_3$ is increased, it becomes slightly broader. As can be seen from the figure the effect of $R_3$ on the MWD of the polymer from batch reactors, in contrast to this, is found to be much more. In figure 4.7 the effect of $R_3$ on the mole fraction distribution of $Q_i$ has been shown. $[Q_{1T}]$ $(= [Q_1] + [Q_1'])$ for HCSTR is found to be much longer than for batch reactor, whereas the remainder of the distribution curve is found to be negligibly affected.

In figure 4.8 and 4.9, the effect of $R_3$ on $\bar{M}_n$ and $\bar{M}_w$ versus time has been examined. As $R_3$ increases, the $\bar{M}_n$ curves rise upwards; however for a given $R_3$ they are always lower than those for batch reactors. It can be noted that for large $R_3$, the reaction at para positions occur with higher likelihood, this way the preferred molecular structure being OH⟨○⟩— $CH_2$—⟨○⟩OH. This leads to the reduction in the polydispersity and gives

considerably lowered $\bar{M}_w$. For the values of $R_3$ studied for HCSTR, in figure 4.9, this is not found to occur even though the curves become close to each other for $R_3$ beyond 5.

In figure 4.10 and 4.11, the effect of $[P]_o / [F]_o$ on the mole fraction distribution of $P_i$ and $Q_i$ have been examined. In figure 4.10, the conversion of phenol (for x=0.20) is always found to be smaller and as a result of which the distribution curves appear steeper than those for batch reactors. Similarly in figure 4.11, $[Q_{1T}]$ $(= [Q_1] + [Q_1'])$ for HCSTR is larger. On calculation of the polydispersity index, $\beta$, of the polymer found in HCSTR is always larger. In table 4.1 and 4.2 the effect of $R_1$ has been examined on the distributions of $P_i$ and $Q_i$ and results compared with those for batch reactors. Similar results are obtained when $R_2$ is varied and the MWD are found to be insensitive to these parameters.

TABLE 4.1

Effect of R1 on $P_n$; R2 = 0.30, R3 =2.40; X=0.90

| R1 | | $P_1$ | $P_2$ | $P_3$ | $P_4$ | $P_5$ | $P_6$ | $P_7$ | $P_8$ | $P_9$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | Batch | 0.2725 | 0.2012 | 0.1099 | 0.0583 | 0.0309 | 0.0163 | 0.0086 | 0.0045 | 0.0024 |
| 0.05 | HCSTR | 0.06233 | 0.1175 | 0.04597 | 0.02336 | 0.01341 | 0.00829 | 0.00538 | 0.0036 | 0.00249 |
| | Batch | 0.2741 | 0.2012 | 0.1092 | 0.0581 | 0.03087 | 0.01637 | 0.00868 | 0.0046 | 0.0024 |
| 0.15 | HCSTR | 0.6234 | 0.1175 | 0.04594 | 0.0234 | 0.0132 | 0.00832 | 0.00543 | 0.00365 | 0.00247 |
| | Batch | 0.2756 | 0.2013 | 0.1084 | 0.058 | 0.03082 | 0.01638 | 0.00871 | 0.0046 | 0.00246 |
| 0.25 | HCSTR | 0.6235 | 0.118 | 0.0461 | 0.024 | 0.0135 | 0.00836 | 0.00546 | 0.00366 | 0.0025 |
| | Batch | 0.2771 | 0.2014 | 0.1077 | 0.05765 | 0.03077 | 0.01639 | 0.00873 | 0.00465 | 0.00248 |
| 0.35 | HCSTR | 0.6239 | 0.1185 | 0.0462 | 0.0241 | 0.0136 | 0.00839 | 0.00548 | 0.00369 | 0.0025 |
| | Batch | 0.2793 | 0.2014 | 0.1066 | 0.0573 | 0.03069 | 0.01641 | 0.00877 | 0.00468 | 0.0025 |
| 0.50 | HCSTR | 0.6240 | 0.1187 | 0.0463 | 0.0244 | 0.01361 | 0.00840 | 0.00548 | 0.00369 | 0.00251 |
| | Batch | 0.2835 | 0.2016 | 0.1097 | 0.0566 | 0.03054 | 0.01642 | 0.00882 | 0.00479 | 0.00252 |
| 0.80 | HCSTR | 0.6241 | 0.1187 | 0.04632 | 0.6245 | 0.01363 | 0.00842 | 0.00548 | 0.00369 | 0.00252 |

Effect of R1 $Q_n$; R2 = 0.30, R3 = 2.4; X =0.9

| | $Q_1$ | $Q_1'$ | $Q_2$ | $Q_3$ | $Q_4$ | $Q_5$ | $Q_6$ | $Q_7$ | $Q_8$ |
|---|---|---|---|---|---|---|---|---|---|
| BATCH | 0.01124 | 0.01656 | 0.01443 | 0.006978 | 0.003713 | 0.001962 | 0.001038 | 0.0005489 | 0.0002904 |
| HCSTR | 0.05215 | 0.006525 | 0.02772 | 0.01130 | 0.005898 | 0.003442 | 0.002148 | 0.001404 | 0.000948 |
| BATCH | 0.01099 | 0.01619 | 0.01406 | 0.006780 | 0.003619 | 0.001917 | 0.001017 | 0.0005393 | 0.0002859 |
| HCSTR | 0.05216 | 0.0065255 | 0.02773 | 0.011305 | 0.0058986 | 0.003448 | 0.0021485 | 0.0014048 | 0.000949 |
| BATCH | 0.01076 | 0.01583 | 0.01371 | 0.006593 | 0.003528 | 0.001874 | 0.0009962 | 0.0005296 | 0.0002816 |
| HCSTR | 0.5217 | 0.006526 | 0.027738 | 0.01131 | 0.005899 | 0.00345 | 0.002149 | 0.001405 | 0.00095 |
| BATCH | 0.01053 | 0.01549 | 0.01338 | 0.006415 | 0.003443 | 0.001833 | 0.0009766 | 0.0005204 | 0.0002773 |
| HCSTR | 0.52178 | 0.006527 | 0.02774 | 0.011318 | 0.005901 | 0.00346 | 0.002150 | 0.001406 | 0.000954 |
| BATCH | 0.01022 | 0.01500 | 0.01291 | 0.006166 | 0.003322 | 0.001774 | 0.0009486 | 0.0005071 | 0.0002711 |
| HCSTR | 0.52180 | 0.006531 | 0.0278 | 0.01132 | 0.005006 | 0.00352 | 0.002155 | 0.0014063 | 0.000955 |
| BATCH | 0.009648 | 0.01413 | 0.01206 | 0.005722 | 0.003104 | 0.001669 | 0.0008972 | 0.0004824 | 0.0002594 |
| HCSTR | 0.53186 | 0.006535 | 0.2784 | 0.01133 | 0.005907 | 0.00354 | 0.002164 | 0.001407 | 0.000958 |

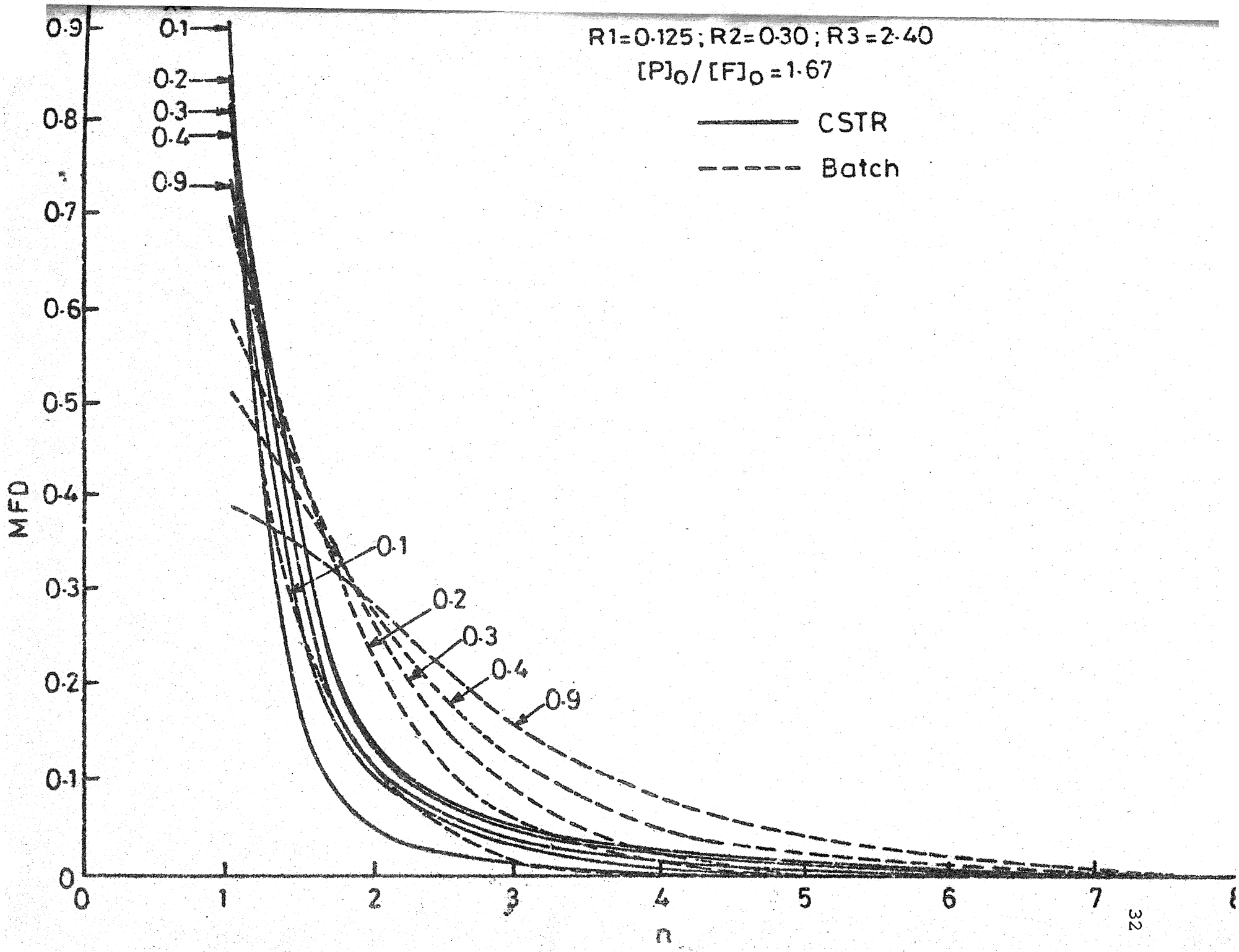
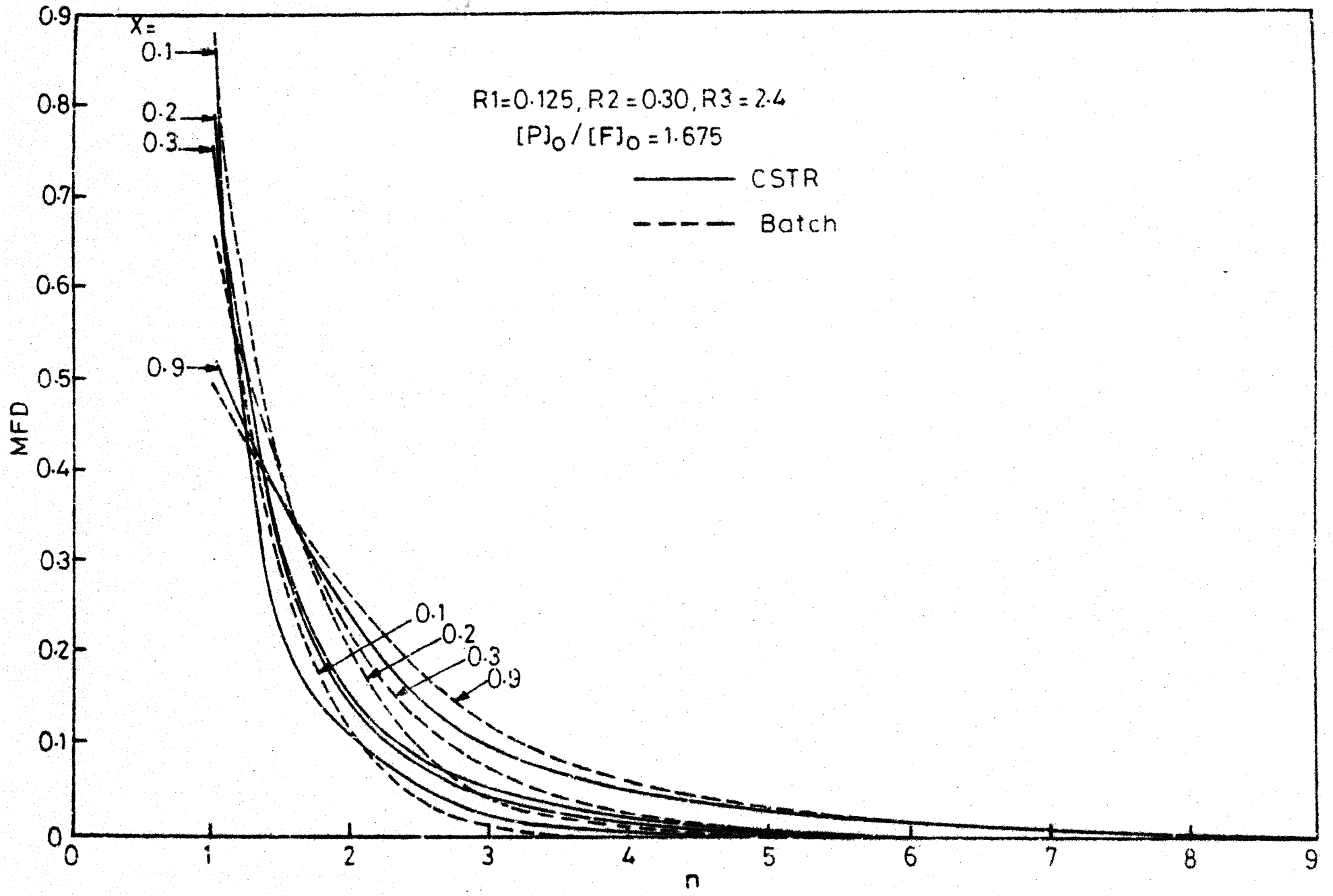



FIGURE 4.1 - Effect of Residence Time on MFD of $P_i$




FIGUR 4.2 - Effect of Residence Time on MFD of $Q_i$

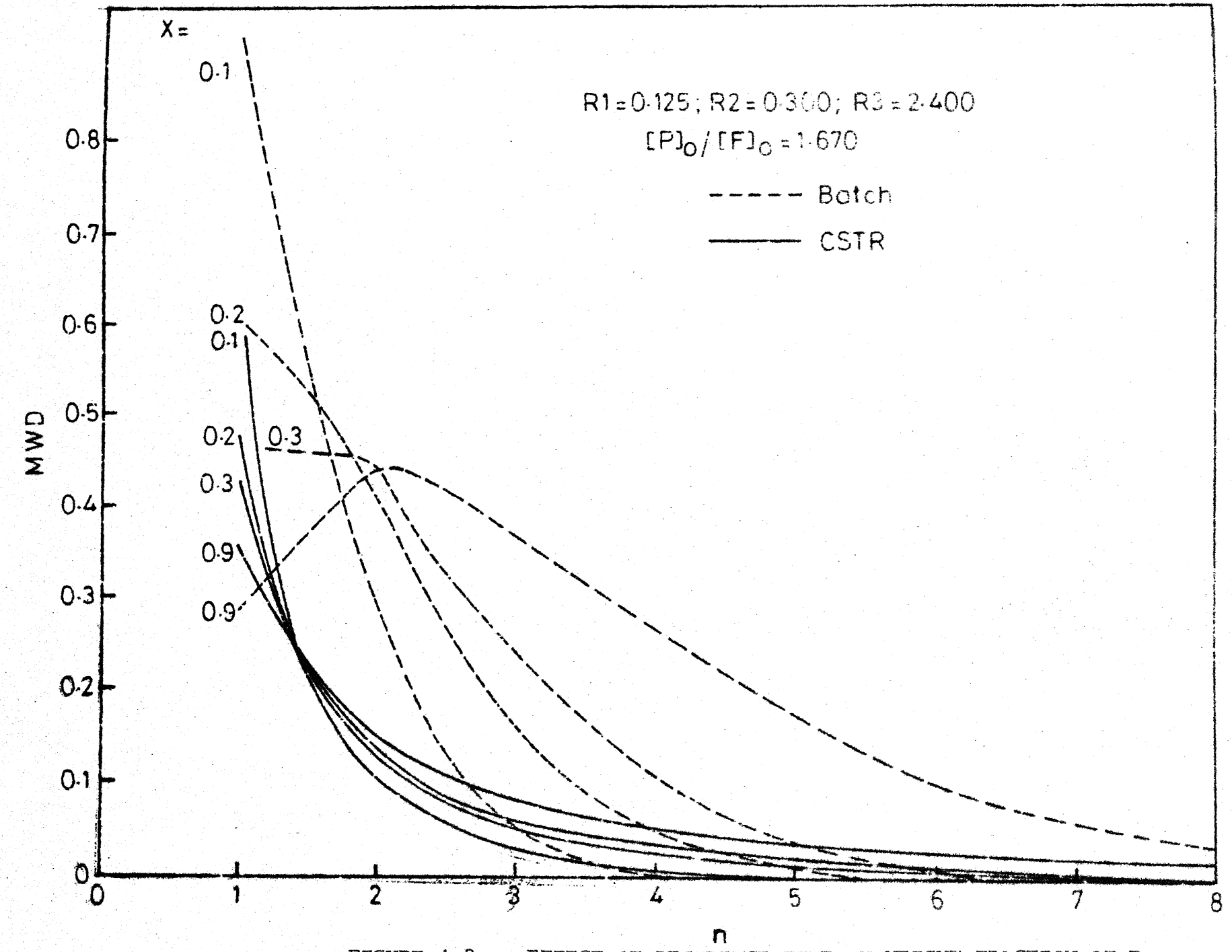



FIGURE 4.3 - EFFECT OF RESIDENCE TIME ON WEIGHT FRACTION OF $P_i$

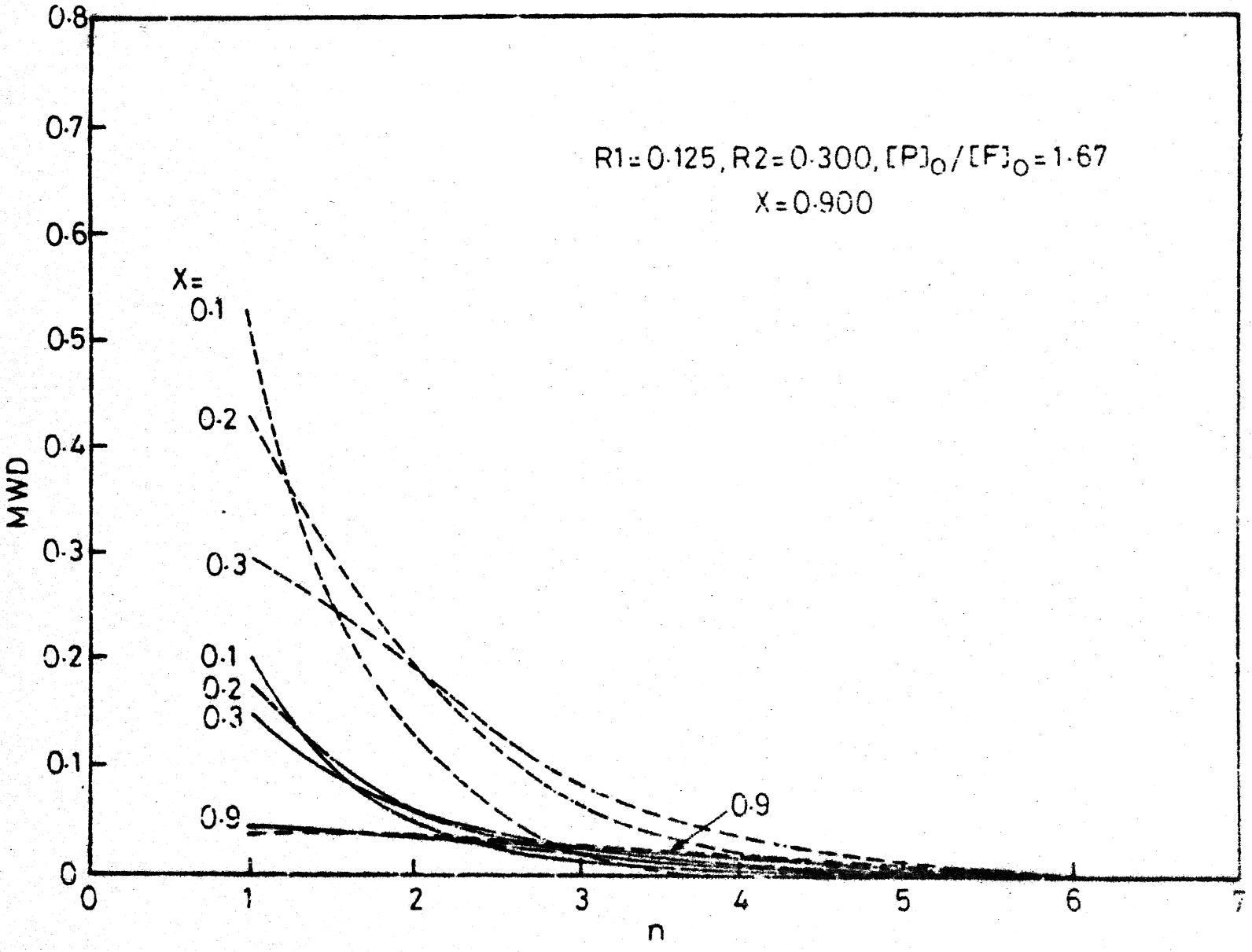



FIGURE 4.4 - Effect of Residence Time on Weight Fraction of $Q_1$

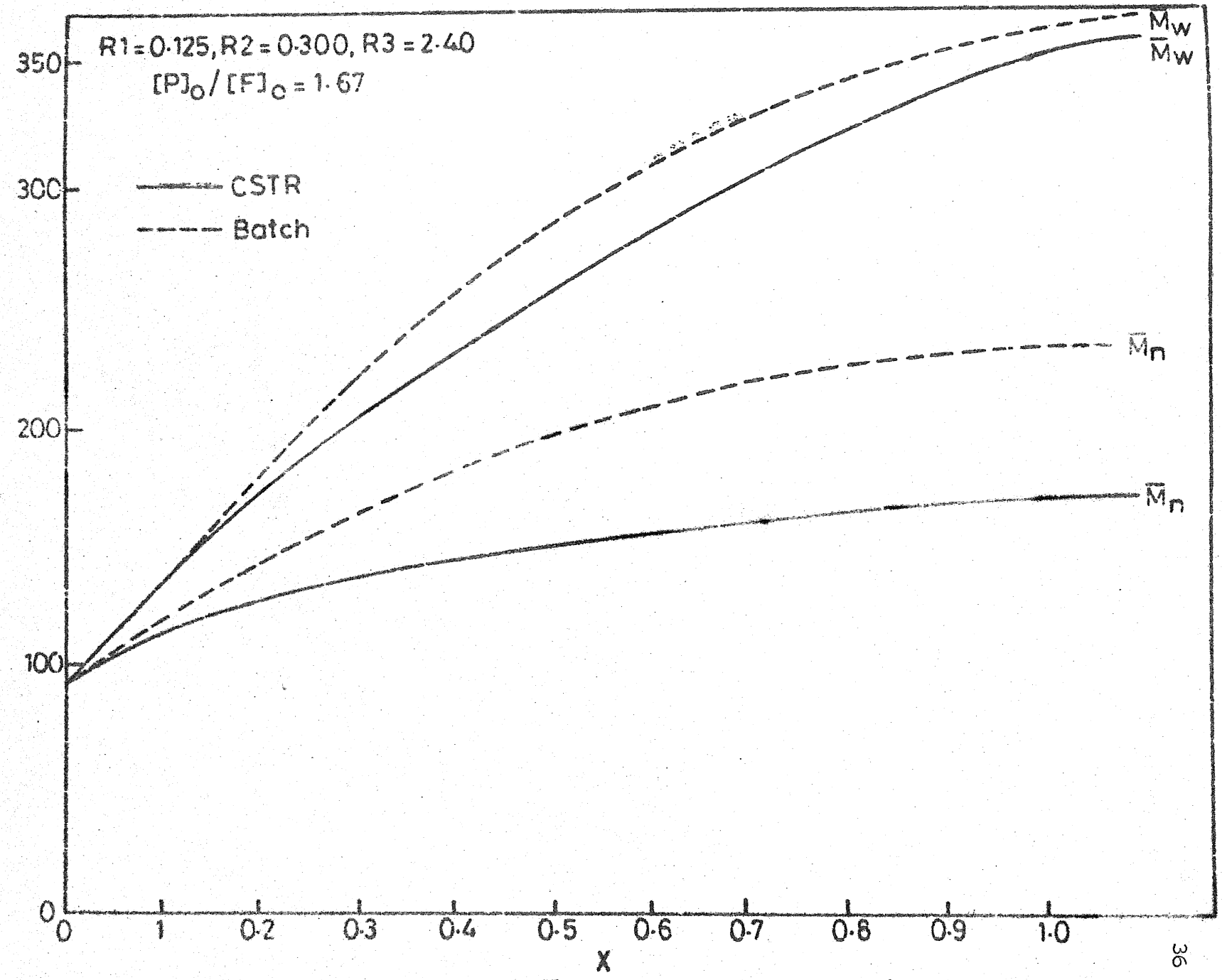



FIGURE 4.5 - $\bar{M}_n$ , $\bar{M}_w$ Versus Dimensionless Time X

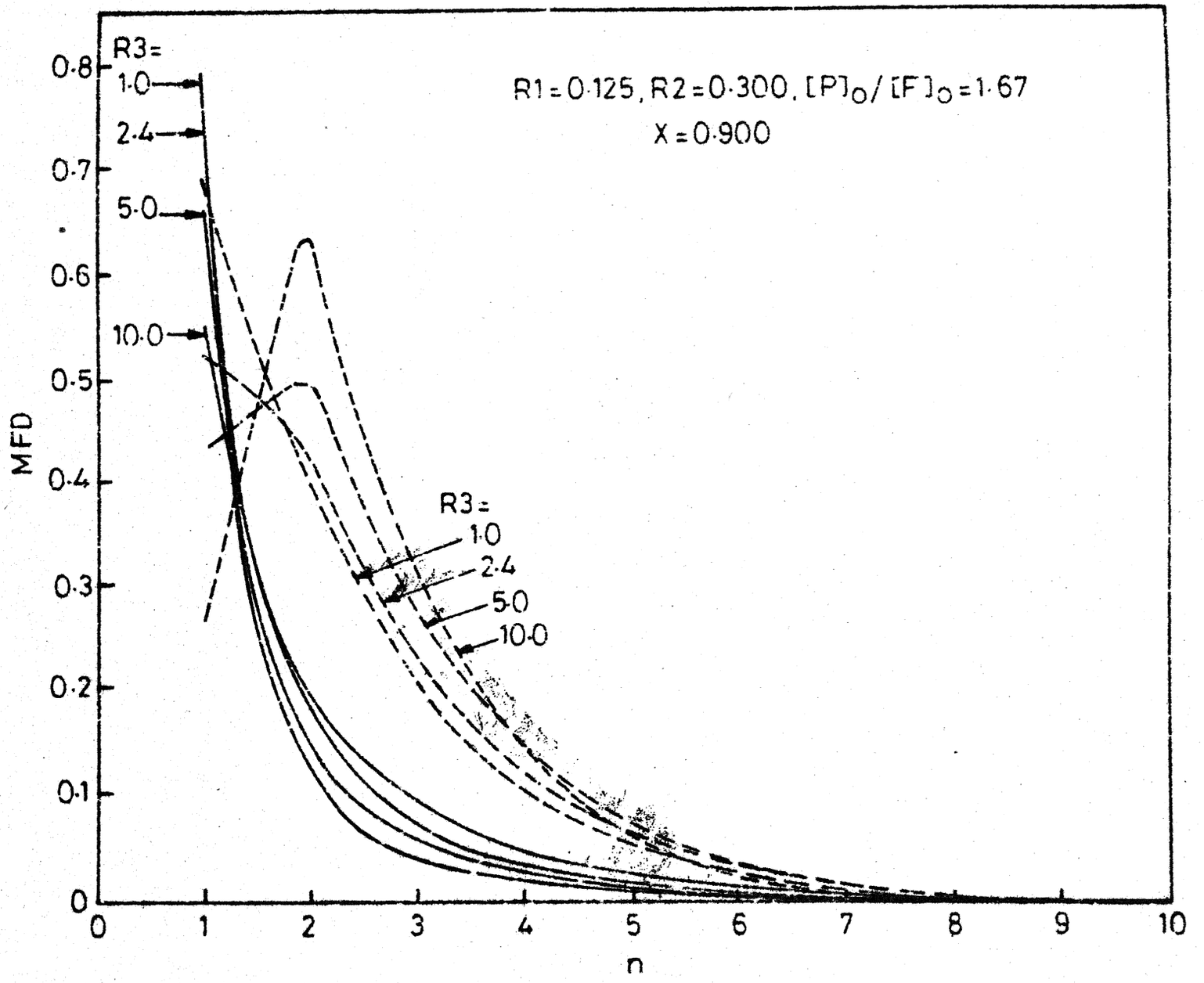



FIGURE 4.6 - Effect of R3 on the MFD of $P_i$

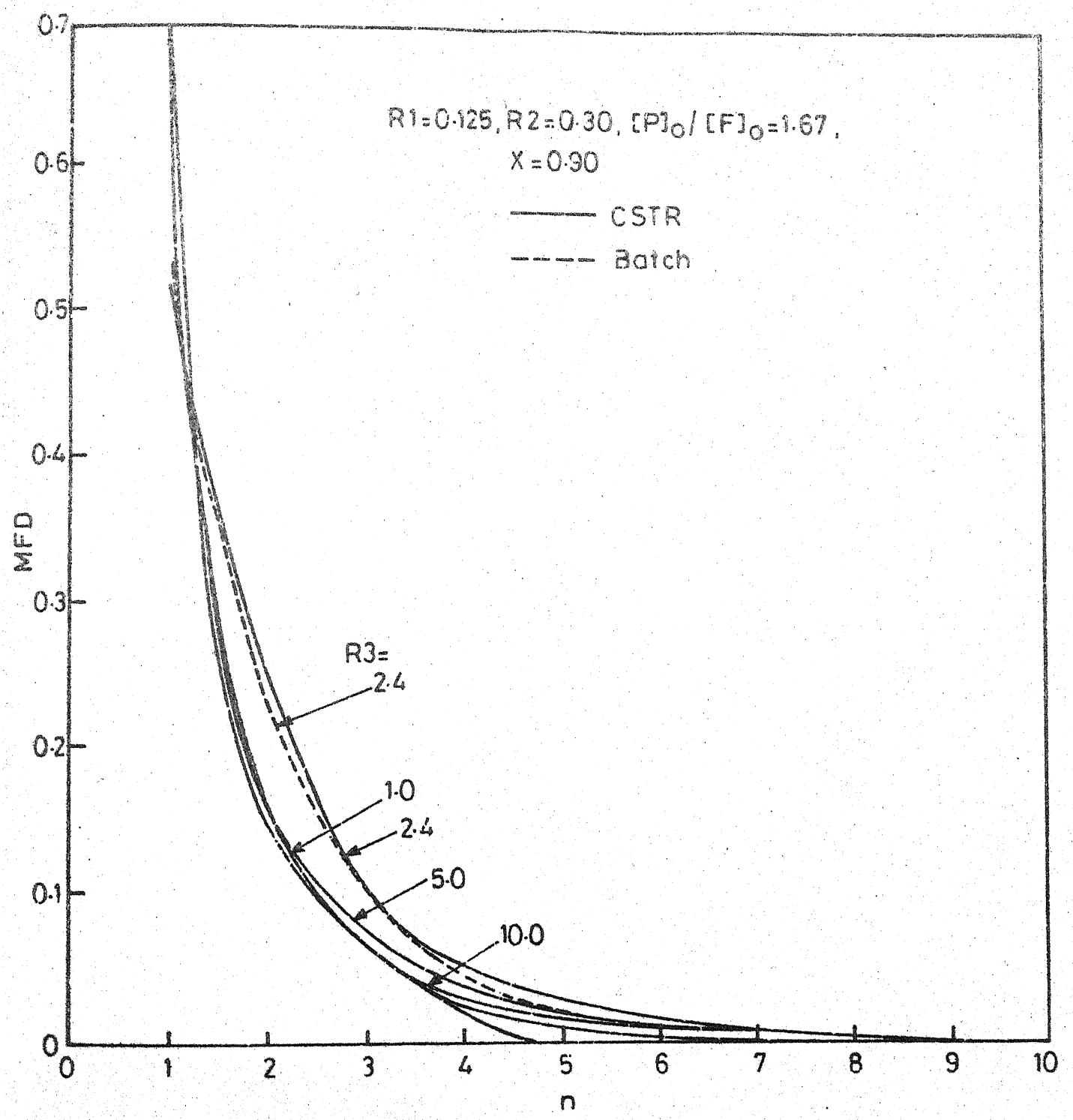



FIGURE 4.7 - Effect of R3 on the MFD of $Q_i$

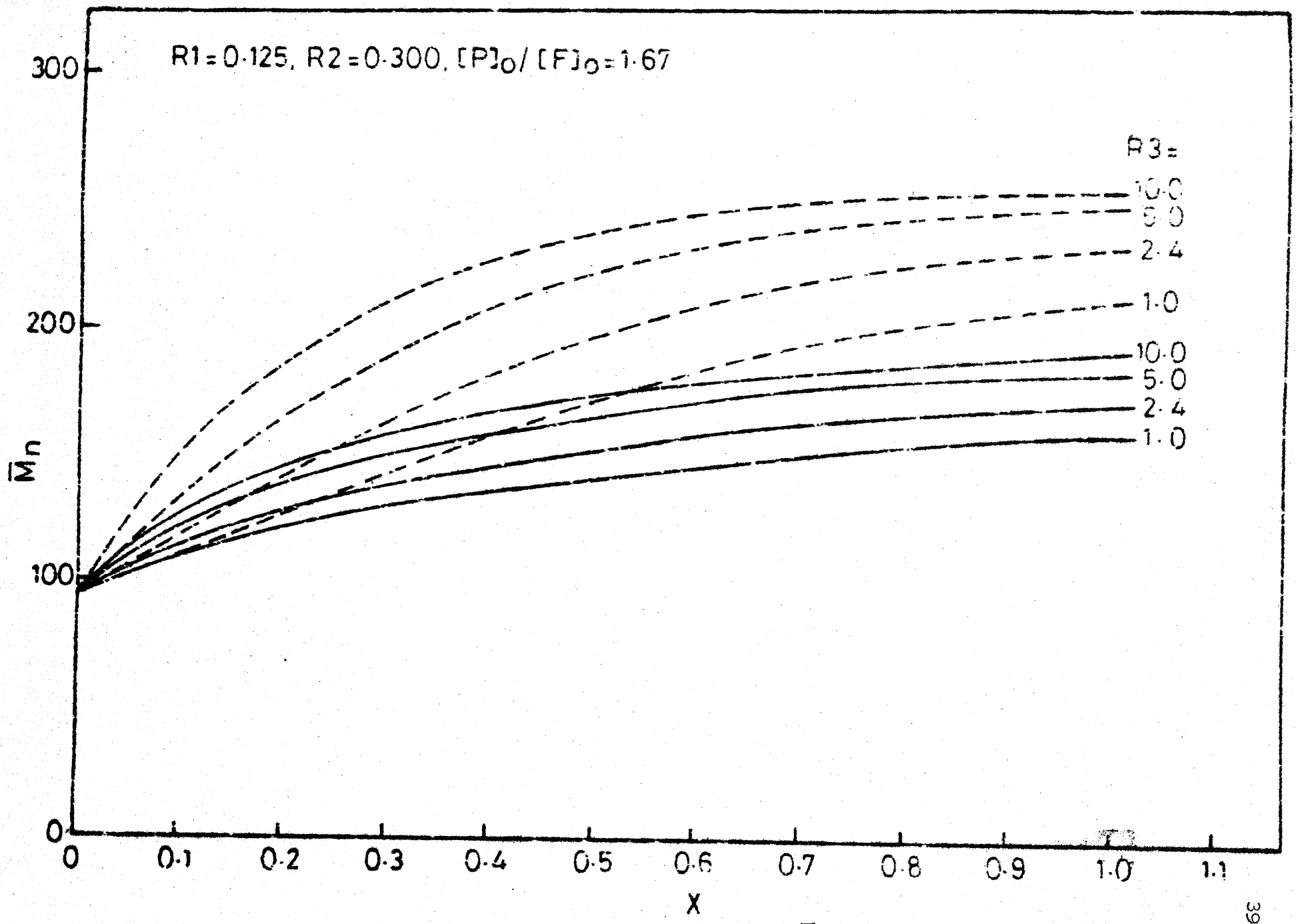



FIGURE 4.8 - Effect of R3 on $\bar{M}_n$

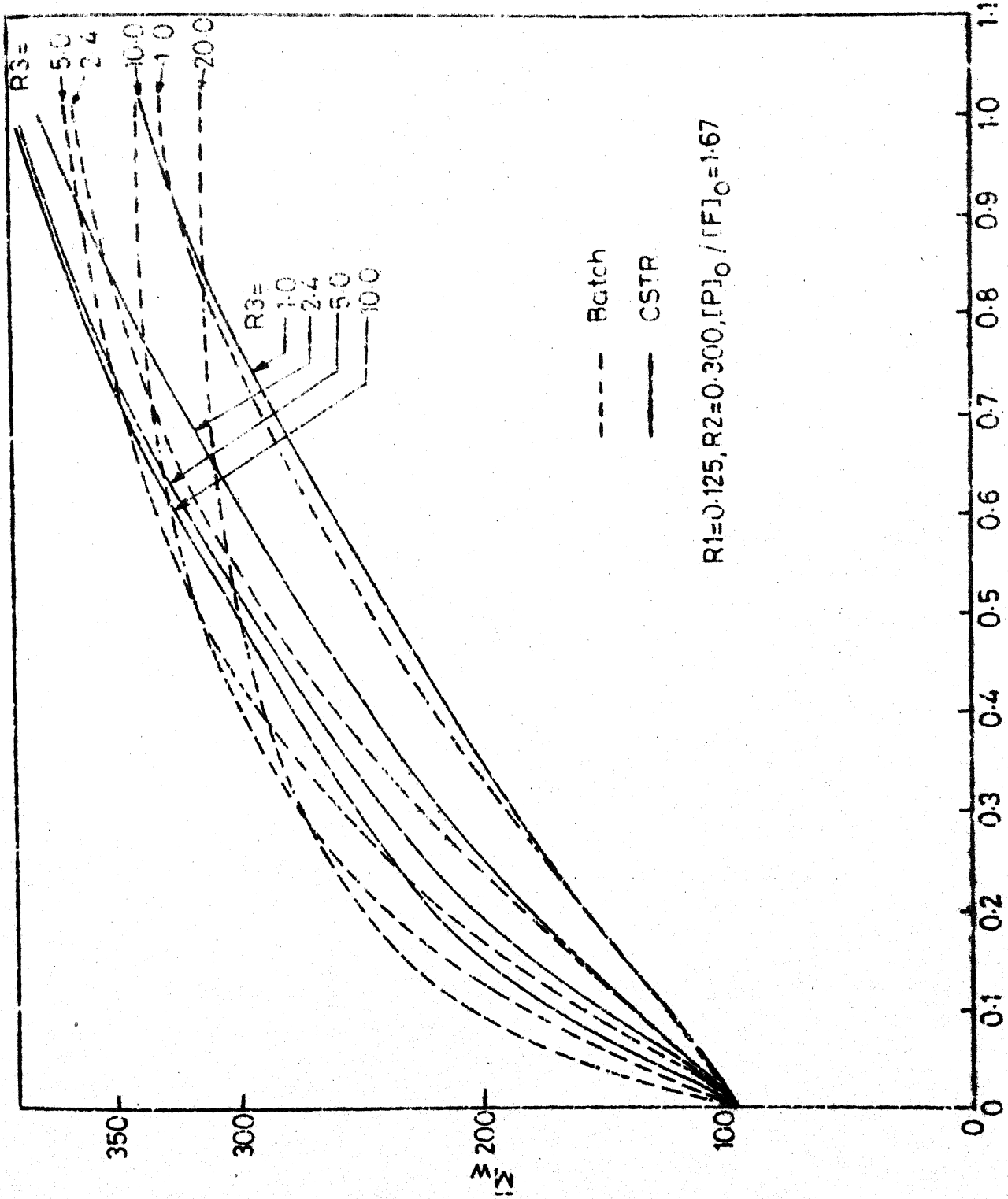



**Fig.9**

FIGURE 4.9 - Effect of R3 on $\overline{M}_w$

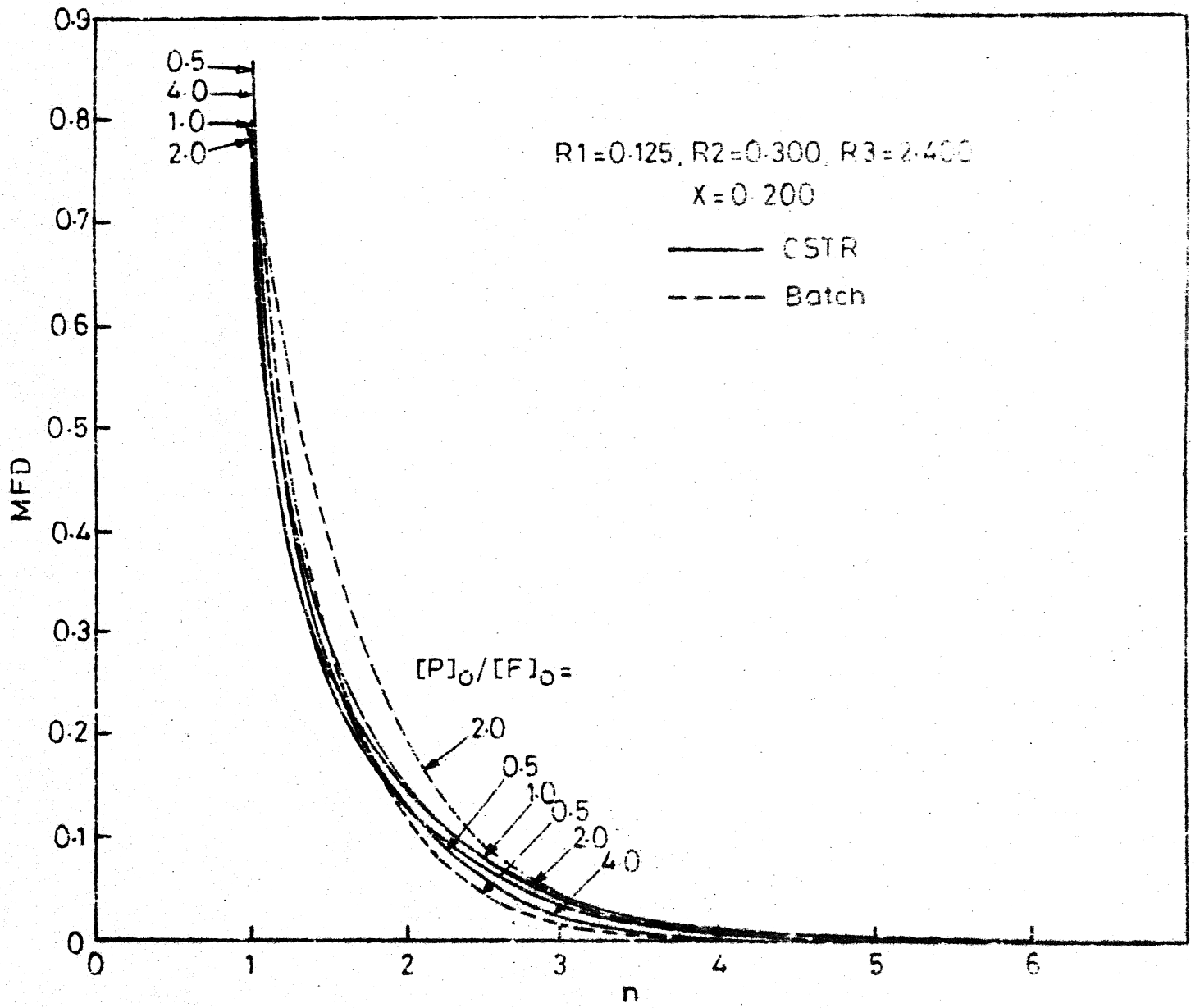



FIGURE 4.10 - Effect of $P_o / F_o$ on the MFD of $P_1$

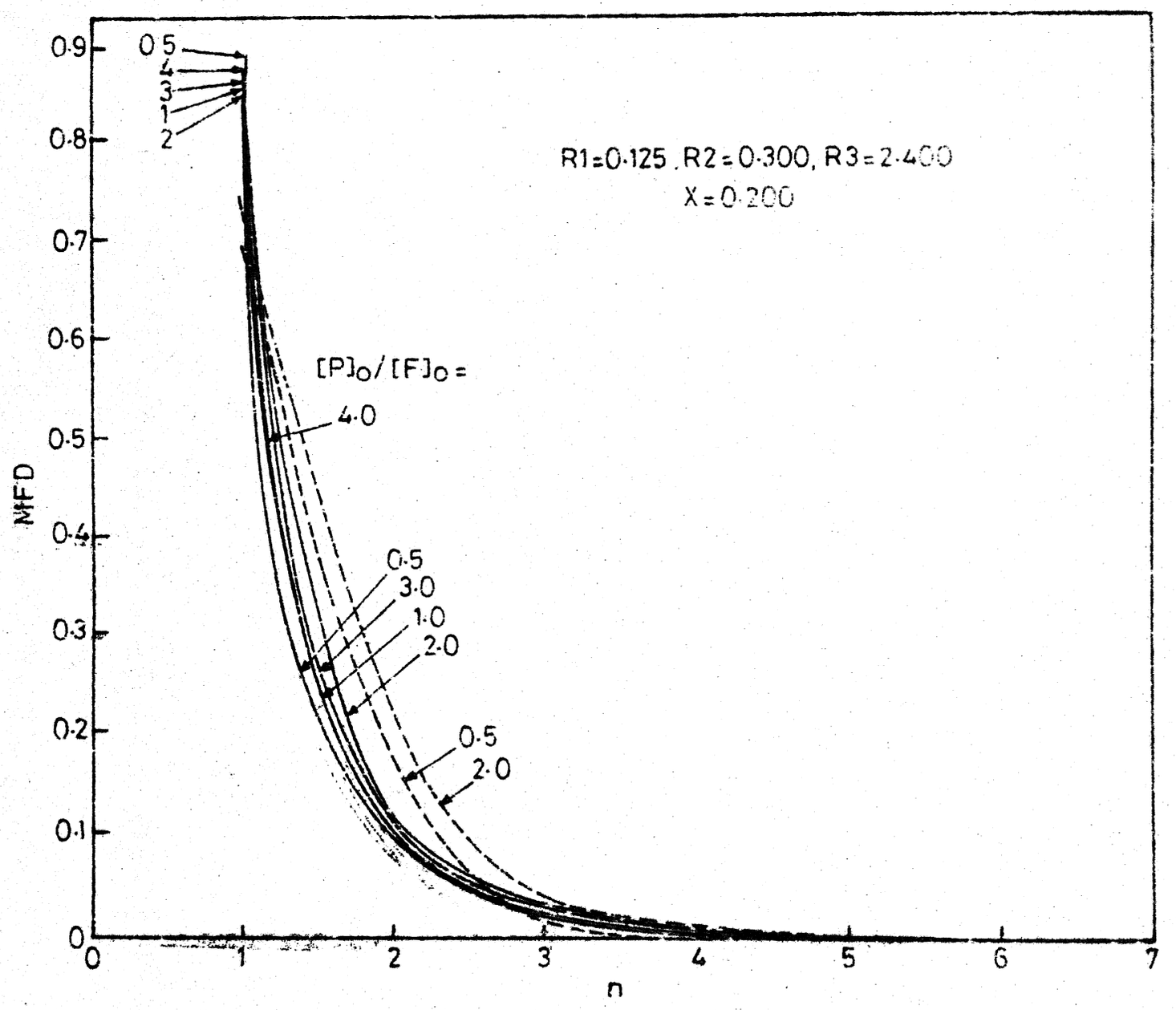


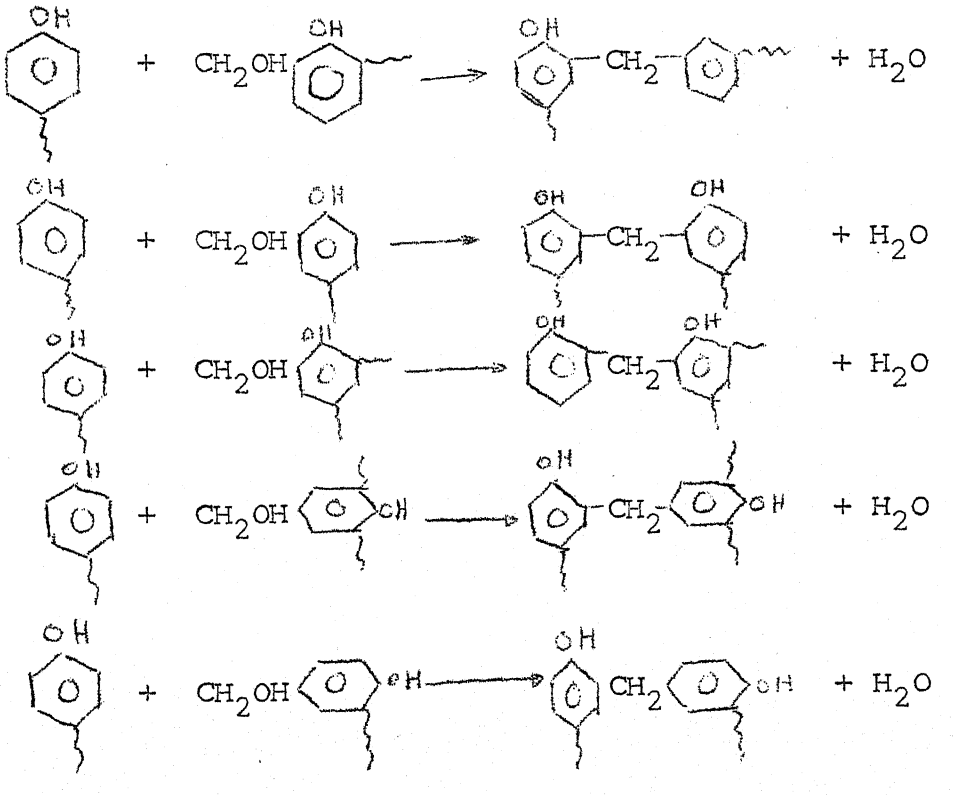

FIGURE 4.11 - Effect of $P_o / F_o$ on the MFD $Q_1$

# CHAPTER 5

## MODEL WITH REVERSIBLE KINETICS

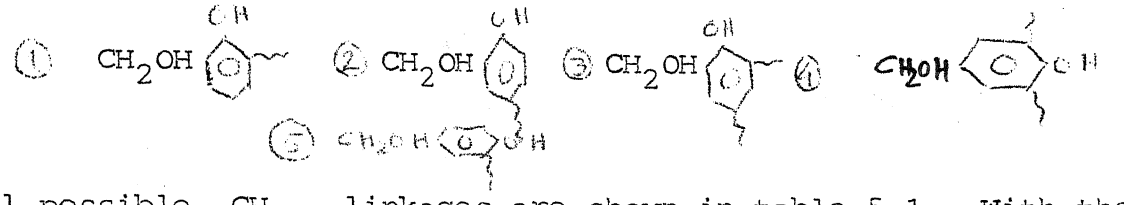
Earlier it was assumed that the condensation product water is removed continuously and hence reverse reactions donot take place. When this is not the case the kinetic model must be modified which is done as follows.

As an example one considers the case when a external $O'_e$ site of any polymer molecule reacts with a bound $-CH_2OH$ group of another polymer molecule. This results in five different $-CH_2-$ linkages as shown below



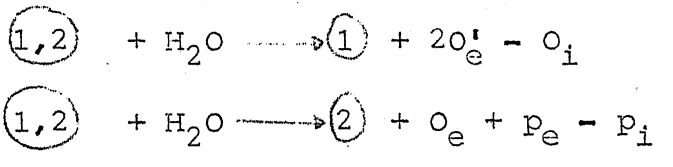
To be able to write the mass balance taking the reverse reactions

into account it is necessary to distinguish the - $CH_2$ - linkages. Therefore the following - $CH_2OH$ groups are distinguished.



All possible -$CH_2$ - linkages are shown in table 5.1. With these the forward reactions between different species are shown in table 5.2. In table 5.3 all reverse reactions are given. It is assumed that $K_5$ represents the rate constant involving - $CH_2$ - and $H_2O$.

A given bond can undergo several reactions for example 1,2 linkage reacts with a water molecule in the following two ways:



Since it can react in two ways a rate constant of $K_5/2$ is assigned to each. This way the rate constant of each bond is decided. On the other hand when a - $CH_2$- linkage react with F, $Q_1$ or $Q_1'$, the nature of the bond gets changed. For example a 1,1 bond becomes 1,4 on reaction with F, $Q_1$ or $Q_1'$ or - $CH_2OH$. The forward reactions involving the interconversion are shown in table 5.4. The state of different sites are not shown in these reactions as it will lead to redundont counting. The reverse

reaction for interconversions of bonds are shown in table 5.5.

One is now in a position to write the mass balance equations for $O_e'$, $O_e$, $O_i$, $P_i$, $P_e$, F, $Q_1$, $Q_1'$, p and balance equations for all the linkages and five bound - $CH_2OH$, in the same way as done earlier.

To get the expression for MWD, the balance equations for all the species $P_n$ and $Q_n$ are written. Terms due to reverse reactions are added to each of the equations derived earlier for the irreversible case and the following equations results.

$$\frac{d[P_n]}{dt} = \frac{CN}{SUM}[P_{n-1}]\left([Q_1]+[Q_1']\right) + \sum_{i=2}^{n-3}\frac{CN}{SUM}[P_{n-1}][Q_i]$$

$$+ \frac{CM}{SUM}[P_2][Q_{n-2}] + (2K_1+K_4)[P][Q_{n-1}]$$

$$- \frac{2CN}{SUM}[P_n][F] - \frac{CN}{SUM}[P_n]\left(\sum_{2}[Q_m]+[Q_1]+[Q_1']\right)$$

$$-(n-1)K_5[P_n][H_2O] + K_5\sum_{i=n+1}[Q_i][H_2O] + 2K_5[H_2O]$$

$$\times \sum_{i=n+1}[P_i], n \geq 5 \qquad \text{(R-1)}$$

$$\frac{d[P_2]}{dt} = (2K_1+K_4)[P]\left([Q_1]+[Q_1']\right) - \frac{2CM}{SUM}[P_2][F]$$

$$- \frac{CM}{SUM}[P_2]\left(\sum_{m=2}[Q_m]+[Q_1]+[Q_1']\right) - K_5[P_2][H_2O]$$

$$+K_5\sum_{i=3}[Q_i][H_2O] + 2K_5[H_2O]\sum_{i=3}[P_i] + K_5[Q_2][H_2O] \qquad \text{(R-.)}$$

$$\frac{d[P_3]}{dt} = \frac{CM}{SUM}[P_2][Q_1] + \frac{CM}{SUM}[P_2][Q_1'] + (2K_1+K_4)[P][Q_2]$$

$$- \frac{2CN}{SUM}[P_3][F] - \frac{CN}{SUM}[P_3]\left(\sum_{m=2}[Q_m] + [Q_1] + [Q_1']\right)$$

$$-2K_5[P_3][H_2O] + K_5[H_2O]\sum_{i=4}[Q_i] + 2K_5[H_2O]\sum_{i=4}[P_i]$$

$$+ K_5[H_2O][Q_3] \qquad (R-3)$$

$$\frac{d[P_4]}{dt} = \frac{CN}{SUM}[P_3]([Q_1] + [Q_1']) + \frac{CM}{SUM}[P_2][Q_2]$$

$$(2K_1+K_4)[P][Q_3] - \frac{2CN}{SUM}[P_4][F]$$

$$- \frac{CN}{SUM}[P_4]\left(\sum_{n=2}[Q_m] + [Q_1] + [Q_1']\right) - 3K_5[H_2O][P_4]$$

$$+K_5[H_2O]\sum_{i=5}[Q_i] + 2K_5[H_2O]\sum_{i=5}[P_i] + K_5[Q_4][H_2O]$$

(R-4)

$$\frac{d\,Q_n}{dt} = -(2K_1+K_4)[Q_n][P] - \left\{CN.[Q_n] + \frac{CN}{SUM}[Q_n]\left(\sum_{m=2}[Q_m]\right.\right.$$

$$\left.\left. + [Q_1] + [Q_1']\right) + [Q_n](2K_1[Q_1'] + K_1[Q_1] + K_4[Q_1])\right\}$$

$$+ \frac{2CN}{SUM}[P_n][F] + \frac{CN}{SUM}\sum_{i=1}^{n-3}[Q_i][Q_{n-i}] + \frac{CM}{SUM}[Q_2][Q_{n-2}$$

$$\frac{CM}{SUM}[Q_i][Q_{n-1}]+(K_1+K_4)[Q_1][Q_{n-1}] + \frac{CN}{SUM}[Q_{n-1}][Q_1'] + 2K_1[Q_1'][Q_{n-1}]$$

$$- K_5[Q_n][H_2O] - K_5[Q_n](n-1)[H_2O] + K_5 \sum_{i=n+1} [Q_i] H_2O$$

$$n \geq 4 \qquad \text{(R-5)}$$

$$\frac{d[Q_3]}{dt} = -(2K_1+K_4)[Q_3][P] - CN[Q_3] - \frac{CN}{SUM}[Q_3]\left(\sum_2 [Q_m] + [Q_1] + [Q_1']\right) - [Q_3](2K_1[Q_1'] + K_1[Q_1] + K_4[Q_1])$$

$$+ \frac{"2CN}{SUM}[P_3][F] + (K_1+K_4)[Q_1][Q_2] + 2K_1[Q_1'][Q_2]$$

$$+ \frac{CM}{SUM}[Q_2]([Q_1] + [Q_1']) - K_5[Q_3][H_2O] - 2K_5[Q_3]$$

$$\times[H_2O] + K_5 \sum_4 [Q_i][H_2O] \qquad \text{(R-6)}$$

$$\frac{d[Q_2]}{dt} = (K_1+K_4)[Q_1]^2 + (3K_1+K_4)[Q_1][Q_1'] + 2K_1[Q_1']^2$$

$$+ \frac{2CM}{SUM}[P_2][F] - (2K_1+K_4)[Q_2][P] - CN[Q_2]$$

$$- \frac{CM}{SUM}[Q_2]\left(\sum_{m=2}[Q_m] + [Q_1] + [Q_1']\right)$$

$$- [Q_2](2K_1[Q_1'] + K_1[Q_1] + K_4[Q_1]) - K_5[Q_2][H_2O]$$

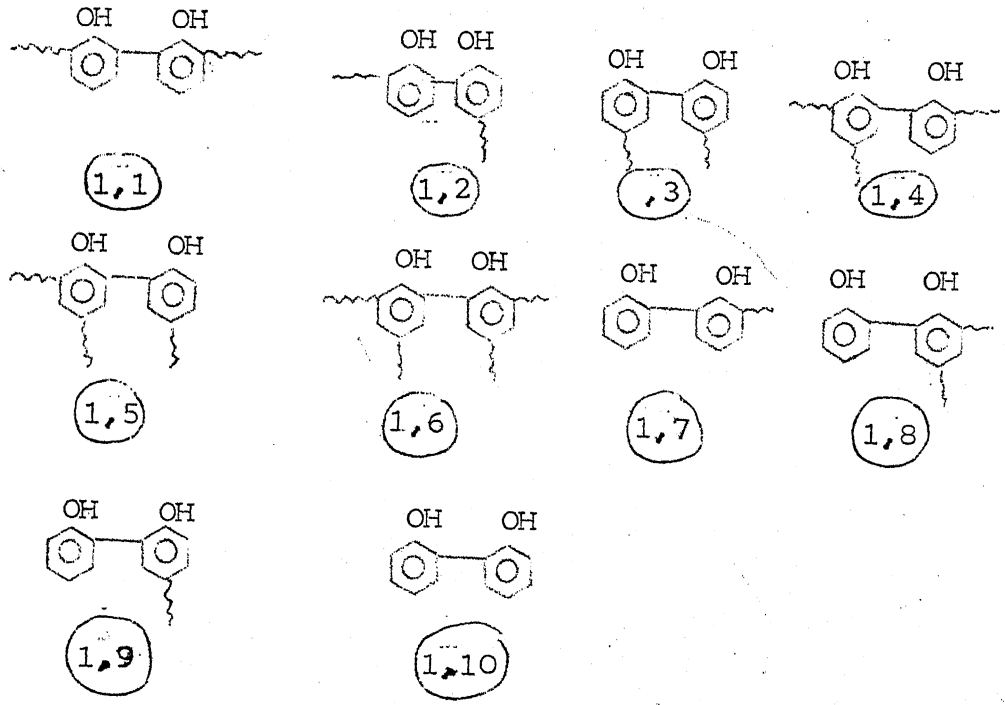
$$- K_5[Q_2][H_2O] + K_5 \sum_{i=3} [Q_i][H_2O] \qquad \text{(R-7)}$$

Equation R-1 is the rate expression for $P_n$, $n \geq 5$. The reverse reaction in which $P_n$ disintegrates contributes the term $(n-1)\, K_5 [P_n] [H_2O]$ for there are (n-1) bonds in $P_n$. $P_n$ can be produced if any $Q_i$ ( $i \geq n+1$) is attacked by a water molecule. Ther term $K_5 \sum_{i=n+1} [Q_i] [H_2O]$ is thus accounted for. On the other hand $P_n$ is also produced when a $P_i$ ( $i \geq n+1$) reacts with water. It can be noted that the breaking of bond from either side of $P_i$ ($i \geq n+1$) will lead to formation of $P_n$ and this leads to the term $2K_5 [H_2O] \sum_{i=n+1} [P_i]$. In similar ways, the equations for other species are written.

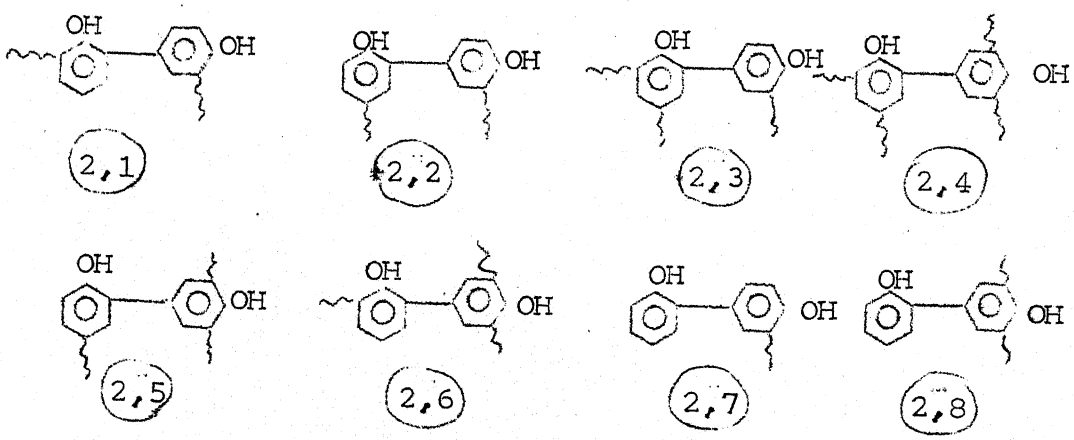
TABLE 5.1

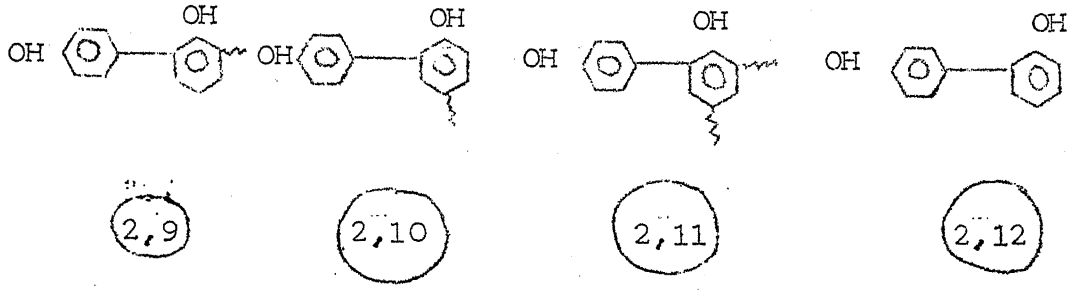
Different Types of $-CH_2-$ Linkages

(a) o-o linkages

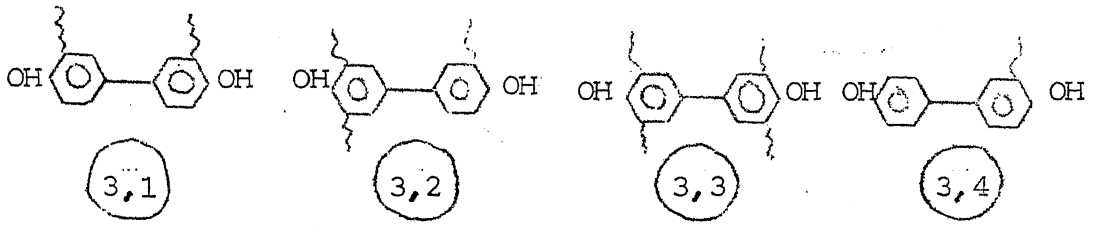


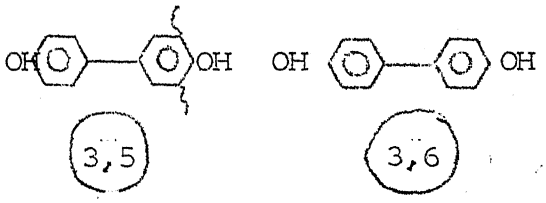

(b) o-p linkages






(c) p–p Linkages



## TABLE 5.2

## FORWARD REACTIONS

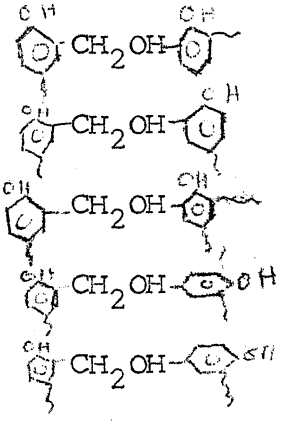
We are not calling a $CH_2OH$ as a bond.

(a) Reactions with F

1. $O_e' + F \xrightarrow{4K_1} (2) - O_e' + O_i + H_2O$
2. $O_e + F \xrightarrow{K_1} (1) - P_e + p_i + H_2O$
3. $O_i + F \xrightarrow{K_2} (3) + H_2O$
4. $p_i + F \xrightarrow{K_3} (4) + H_2O$
5. $p_e + F \xrightarrow{K_4} (5) + O_i - O_e + H_2O$

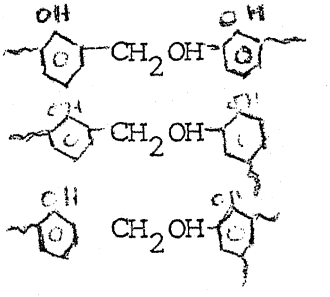
(b) $O_e'$ with $CH_2OH$

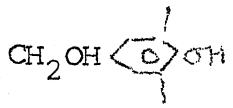
1. $O_e' + (1) \xrightarrow{2K_1} (1,2) + O_i - O_e' + H_2O$
2. $O_e' + (2) \xrightarrow{2K_1} (1,3) + O_i - O_e' + H_2O$
3. $O_e' + (3) \xrightarrow{2K_1} (1,5) + O_i - O_e' + H_2O$
4. $O_e' + (4) \xrightarrow{2K_1} (2,5) + O_i - O_e' + H_2O$
5. $O_e' + (5) \xrightarrow{2K_1} (2,2) + O_i - O_e' + H_2O$

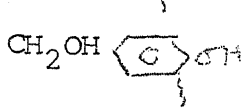


(c) $O_e$ with $CH_2OH$

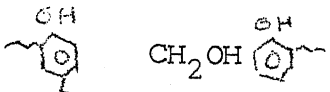
1. $O_e + (1) \xrightarrow{K_1} (1,1) + p_i - p_e + H_2O$
2. $O_e + (2) \xrightarrow{K_1} (1,2) + p_i - p_e + H_2O$
3. $O_e + (3) \xrightarrow{K_1} (1,4) + p_i - p_e + H_2O$

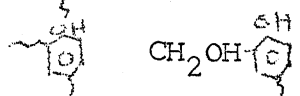


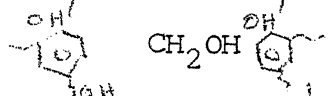
4. $O_e$ + (4) $\xrightarrow{K_1}$ (2,6) $+p_i-p_e+H_2O$  

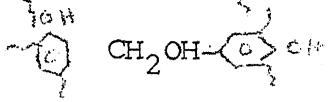
5. $O_e$ + (5) $\xrightarrow{K_1}$ (2,1) $+ p_i-p_e+H_2O$  

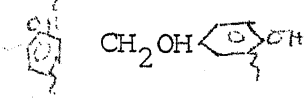
(d) $O_i$ with $CH_2OH$

1. $O_i$ + (1) $\xrightarrow{K_2}$ (1,4) $+ H_2O$ 

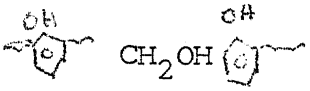
2. $O_i$ + (2) $\xrightarrow{K_2}$ (1,5) $+ H_2O$ 

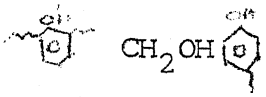
3. $O_i$ + (3) $\xrightarrow{K_2}$ (1,6) $+ H_2O$ 

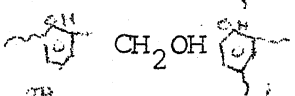
4. $O_i$ + (4) $\xrightarrow{K_2}$ (2,4) $+ H_2O$ 

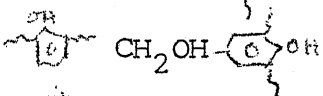
5. $O_i$ + (5) $\xrightarrow{K_2}$ (2,3) $+ H_2O$ 

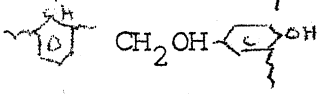
(e) $P_i$ with $CH_2OH$

1. $p_i$ + (1) $\xrightarrow{K_3}$ (2,6) $+ H_2O$ 

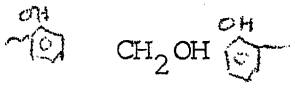
2. $p_i$ + (2) $\xrightarrow{K_3}$ (2,5) $+ H_2O$ 

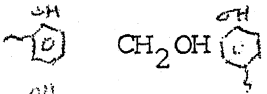
3. $p_i$ + (3) $\xrightarrow{K_3}$ (2,4) $+ H_2O$ 

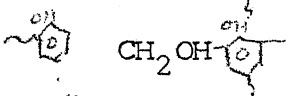
4. $p_i$ + (4) $\xrightarrow{K_3}$ (3,3) $+ H_2O$ 

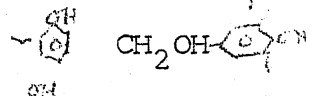
5. $p_i$ + (5) $\xrightarrow{K_3}$ (3,2) $+ H_2O$ 

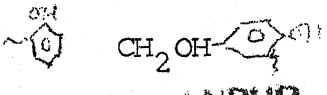
(f) $P_e$ with $CH_2OH$

1. $p_e$ + (1) $\xrightarrow{K_4}$ (2,1) $+ o_i-o_e+H_2O$ 

2. $p_e$ + (2) $\xrightarrow{K_4}$ (2,2) $+ o_i-o_e+H_2O$ 

3. $p_e$ + (3) $\xrightarrow{K_4}$ (2,3) $+ o_i-o_e+H_2O$ 

4. $p_e$ + (4) $\xrightarrow{K_4}$ (3,2) $+ o_i-o_e+H_2O$ 

5. $p_e$ + (5) $\xrightarrow{K_4}$ (3,1) $+ o_i-o_e+H_2O$ 

(g) Rxn of P with F and $CH_2OH$

1. $P + F \xrightarrow{4K_1} Q_1 + H_2O$

   $P + F \xrightarrow{2K_4} Q_1' + H_2O$

2. $P + (1) \xrightarrow{2K_1} (1,7) + O_e + p_e + H_2O$

3. $P + (2) \xrightarrow{2K_1} (1,9) + O_e + p_e + H_2O$

4. $P + (3) \xrightarrow{2K_1} (1,8) + O_e + p_e + H_2O$

5. $P + (4) \xrightarrow{2K_1} (2,8) + O_e + p_e + H_2O$

6. $P + (5) \xrightarrow{2K_1} (2,7) + O_e + p_e + H_2O$

7. $P + (1) \xrightarrow{K_4} (2,9) + 2O_e' + H_2O$

8. $P + (2) \xrightarrow{K_4} (2,10) + 2O_e' + H_2O$

9. $P + (3) \xrightarrow{K_4} (2,11) + 2O_e' + H_2O$

10. $P + (4) \xrightarrow{K_4} (3,5) + 2O_e' + H_2O$

11. $P + (5) \xrightarrow{K_4} (3,4) + 2O_e' + H_2O$

(h) Rxns of P with $Q_1$ and $Q_1'$

1. $P + Q_1' \xrightarrow{2K_1} P_e + 2O_e' + O_e + H_2O + (2,12)$

2. $P + Q_1' \xrightarrow{K_4} (3,6) + 4O_e' + H_2O$

3. $P + Q_1 \xrightarrow{2K_1} (1,10) + 2p_e + 2O_e + H_2O$

4. $P + Q_1 \xrightarrow{K_4} (2,12) + O_e + p_e + 2O_e' + H_2O$

(i) Rxns of $Q_1$ and $Q_1'$ with sites

1. $O_e' + Q_1' \xrightarrow{K_1} O_i + 2O_e' - O_e' + (2,10) + H_2O$

2. $O_e' + Q_1 \xrightarrow{K_1} 1,9 + p_e + O_e + O_i - O_e' + H_2O$

3. $O_e + Q_1' \xrightarrow{K_1} 2,9 + 2O_e' + p_i - p_e + H_2O$

4. $O_e + Q_1 \xrightarrow{K_1} (1,7) + O_e + p_e + p_i + H_2O - p_e$

5. $p_i + Q_1' \xrightarrow{K_3} (2O_e') + 3,5 + H_2O$

6. $p_i + Q_1 \xrightarrow{K_3} (2,8) + O_e + p_e + H_2O$

7. $O_i + Q_1' \xrightarrow{K_2} (2,11) + 2O_e' + H_2O$

8. $O_i + Q_1 \xrightarrow{K_2} (1,8) + O_e + p_e + H_2O$

9. $p_e + Q_1' \xrightarrow{K_4} (3,4) + O_i - O_e + 2O_e' + H_2O$

10. $p_e + Q_1 \xrightarrow{K_4} (2,7) + O_e + p_e + O_i - O_e + H_2O$

(j) Rxns of $Q_1$ and $Q_1'$ with $CH_2OH$

1. $Q_1 + (1) \xrightarrow{K_3} (2,7) + Q_e + p_e - p_i + (3)$

$\xrightarrow{K_1} (1,1) + (1) + p_i$

$\xrightarrow{K_4} (2,1) + (2) + O_i$

2. $Q_1 + 2 \xrightarrow{K_2} (1,8) + H_2O - O_i + (3) + O_e + p_e$

$\xrightarrow{K_1} (1,2) + H_2O + p_i + (1)$

$\xrightarrow{K_4} (2,2) + H_2O + O_i + (2)$

3. $Q_1 + 3 \xrightarrow{K_4} (1,5) + H_2O + p_i + (1)$

$\xrightarrow{K_4} (2,3) + H_2O + O_i + (2)$

4. $Q_1 + (4) \xrightarrow{K_1} (2,6) + H_2O + p_i + (1)$

$\xrightarrow{K_4} (3,2) + H_2O + o_i + (2)$

5. $Q_1 + (5) \xrightarrow{K_2} (1,8) + H_2O - o_i + (4) + o_e + p_e$

$\xrightarrow{K_1} (2,1) + H_2O + p_i + (1)$

$\xrightarrow{K_4} (3,1) + H_2O + o_i + (2)$

6. $Q_1' + (1) \xrightarrow{2K_1} (1,2) + H_2O + o_i + (5)$

$\xrightarrow{K_3} (3,5) + H_2O + 2o_e' - p_i + (3)$

7. $Q_1' + (2) \xrightarrow{2K_1} (1,3) + H_2O + o_i + (5)$

$\xrightarrow{K_2} (2,11) + H_2O - o_i + 2o_e' + (3)$

8. $Q_1' + (3) \xrightarrow{2K_1} (1,5) + H_2O + o_i + (5)$

9. $Q_1' + (4) \xrightarrow{2K_1} (2,5) + H_2O + o_i + (5)$

10. $Q_1' + (5) \xrightarrow{2K_1} (2,2) + H_2O + o_i + (5)$

$\xrightarrow{K_2} (2,11) + H_2O - o_i + 2o_e' + (4)$

11. $Q_1 + Q_1' \xrightarrow{2K_1} (1,9) + H_2O + o_e + p_e + o_i + (5)$

$\xrightarrow{K_1} (2,9) + H_2O + 2o_e' + p_i + (1)$

$\xrightarrow{K_4} (3,4) + H_2O + 2o_e' + o_i + (2)$

12. $Q_1 + Q_1 \xrightarrow{2K_1} (1,7) + H_2O + o_e + p_e + p_i + (1)$

$\xrightarrow{2K_4} (2,7) + H_2O + o_e + p_e + o_i + (2)$

13. $Q_1' + Q_1' \xrightarrow{4K_1} (2,10) + 2o_e' + o_i + 5$

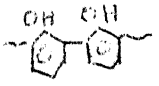
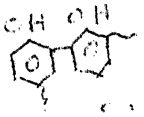
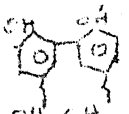
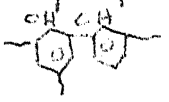
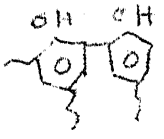
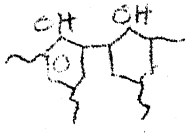
TABLE 5.3

REVERSE REACTIONS

(a) With $-CH_2OH$

1. (1) + $H_2O$ $\xrightarrow{K_5}$ $F + O_e + p_e - p_i$
2. (2) + $H_2O$ $\xrightarrow{K_5}$ $2O'_e + F - O_i$
3. (3) + $H_2O$ $\xrightarrow{K_5}$ $O_i + F$
4. (4) + $H_2O$ $\xrightarrow{K_5}$ $p_i + F$
5. (5) + $H_2O$ $\xrightarrow{K_5}$ $O_e + p_e - O_i + F$

(b) With $-CH_2-$ Linkages

1.  (1,1) + $H_2O$ $\xrightarrow{K_5}$ (1) + $O_e + p_e - p_i$
2.  (1,2) + $H_2O$ $\xrightarrow{\frac{1}{2}K_5}$ (1) + $2O'_e - O_i$
   $\xrightarrow{\frac{1}{2}K_5}$ (2) + $O_e + p_e - p_i$
3.  (1,3) + $H_2O$ $\xrightarrow{K_5}$ (2) + $2O'_e - O_i$
4.  (1,4) + $H_2O$ $\xrightarrow{\frac{1}{2}K_5}$ (1) + $O_i$
   $\xrightarrow{\frac{1}{2}K_5}$ (3) + $O_e + p_e - p_i$
5.  (1,5) + $H_2O$ $\xrightarrow{\frac{1}{2}K_5}$ (2) + $O_i$
   $\xrightarrow{\frac{1}{2}K_5}$ (3) + $2O'_e - O_i$
6.  (1,6) + $H_2O$ $\xrightarrow{K_5}$ (3) + $O_i$

7. 

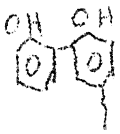
$(1,7) + H_2O \xrightarrow{\frac{1}{2}K_5} Q_1 - O_e - P_e + O_e + P_e - P_i$

$\xrightarrow{\frac{1}{2}K_5} P - O_e - P_e + (1)$

8. 

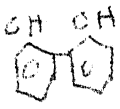
$(1,8) + H_2O \xrightarrow{\frac{1}{2}K_5} Q_1 - O_e - P_e + O_i$

$\xrightarrow{\frac{1}{2}K_5} (3) - O_e - P_e + P$

9. 

$(1,9) + H_2O \xrightarrow{\frac{1}{2}K_5} Q_1 - O_e - P_e + 2O_e - O_i$

$\xrightarrow{\frac{1}{2}K_5} P + (2) - O_e - P_e$

10. 

$(1,10) + H_2O \xrightarrow{K_5} 2Q_1 - 2O_e - 2P_e$

11. 

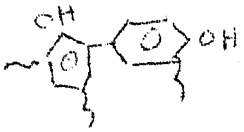
$(2,1) + H_2O \xrightarrow{\frac{1}{2}K_5} (1) + O_e + P_e - O_i$

$\xrightarrow{\frac{1}{2}K_5} (5) + O_e + P_e - P_i$

12. 

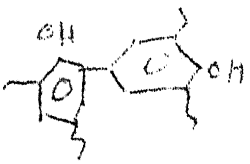
$(2,2) + H_2O \xrightarrow{\frac{1}{2}K_5} (2) + O_e + P_e - O_i$

$\xrightarrow{\frac{1}{2}K_5} (5) + 2O_e' - O_i$

13. 

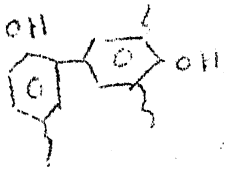
$(2,3) + H_2O \xrightarrow{\frac{1}{2}K_5} (3) + O_e + P_e - O_i$

$\xrightarrow{\frac{1}{2}K_5} (5) + O_i$

14. 

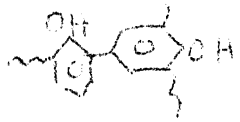
$(2,4) + H_2O \xrightarrow{\frac{1}{2}K_5} (4) + O_i$

$\xrightarrow{\frac{1}{2}K_5} (3) + P_i$

15. 

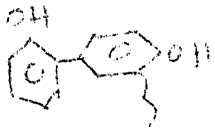
$(2,5) + H_2O \xrightarrow{\frac{1}{2}K_5} (4) + 2O_e' - O_i$

$\xrightarrow{\frac{1}{2}K_5} (2) + P_i$

16. 

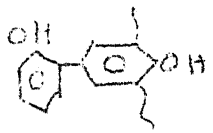
$$\textcircled{2,6} + H_2O \xrightarrow{\frac{1}{2}K_5} \textcircled{1} + p_i$$

$$\xrightarrow{\frac{1}{2}K_5} \textcircled{4} + O_e + p_e - p_i$$

17. 

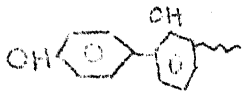
$$\textcircled{2,7} + H_2O \xrightarrow{\frac{1}{2}K_5} Q_1 - O_e - p_e + O_e + p_e - O_i$$

$$\xrightarrow{\frac{1}{2}K_5} P - O_e - p_e + \textcircled{5}$$

18. 

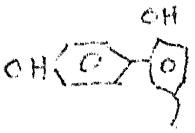
$$\textcircled{2,8} + H_2O \xrightarrow{\frac{1}{2}K_5} \textcircled{4} + P - O_e - p_e$$

$$\xrightarrow{\frac{1}{2}K_5} Q_1 - O_e - p_e + p_i$$

19. 

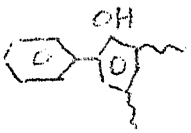
$$\textcircled{2,9} + H_2O \xrightarrow{\frac{1}{2}K_5} Q_1' + O_e + p_e - p_i - 2O_e'$$

$$\longrightarrow P + \textcircled{1} - 2O_e'$$

20 

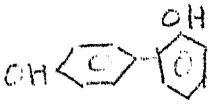
$$\textcircled{2,10} + H_2O \xrightarrow{\frac{1}{2}K_5} \textcircled{2} + P - 2O_e'$$

$$\xrightarrow{\frac{1}{2}K_5} Q_1' + 2O_e' - O_i - 2O_e'$$

21. 

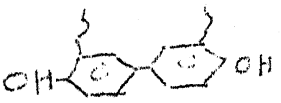
$$\textcircled{2,11} + H_2O \xrightarrow{\frac{1}{2}K_5} Q_1' - 2O_e' + O_i$$

$$\xrightarrow{\frac{1}{2}K_5} P - 2O_e' + \textcircled{3}$$

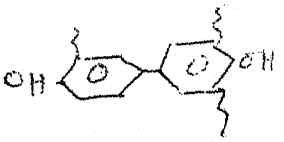
22. 

$$\textcircled{2,12} + H_2O \xrightarrow{\frac{1}{2}K_5} Q_1' - 2O_e' - O_e - p_e + P$$

$$\xrightarrow{\frac{1}{2}K_5} Q_1 - 2O_e' - O_e - p_e + P$$

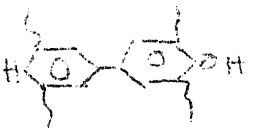
23. 

$$\textcircled{3,1} + H_2O \xrightarrow{K_5} \textcircled{5} + O_e + p_e - O_i$$

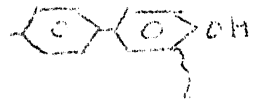
24. 

$$\textcircled{3,2} + H_2O \xrightarrow{\frac{1}{2}K_5} \textcircled{4} + O_e + p_e - O_i$$

$$\xrightarrow{\frac{1}{2}K_5} \textcircled{5} + p_i$$

25. 

(3,3) + $H_2O$ $\xrightarrow{K_5}$ (4) + $p_i$

26. 

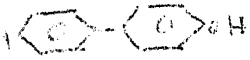
(3,4) + $H_2O$ $\xrightarrow{\frac{1}{2}K_5}$ $Q_1' - 2o_e' + o_e + p_e - o_i$

$\xrightarrow{\frac{1}{2}K_5}$ $P - 2o_e'$ + (5)

27. 

(3,5) + $H_2O$ $\xrightarrow{\frac{1}{2}K_5}$ $Q_1' - 2o_e' + p_i$

$\xrightarrow{\frac{1}{2}K_5}$ $P - 2o_e'$ + (4)

28. 

(3,6) + $H_2O$ $\xrightarrow{K_5}$ $2Q_1' - 4o_e'$

## TABLE 5.4

### Interconversions of Bonds

CX Stands for sum of $-CH_2OH, F, Q_1, Q_1'$

1. (1,1) + CX $\xrightarrow{2K_3}$ (1,4) + $H_2O$
2. (1,2) + CX $\xrightarrow{K_2}$ (1,4) + $H_2O$
   $\xrightarrow{K_3}$ (1,5) + $H_2O$
3. (1,3) + CX $\xrightarrow{2K_2}$ (1,5) + $H_2O$
4. (1,4) + CX $\xrightarrow{K_3}$ (1,6) + $H_2O$
5. (1,5) + CX $\xrightarrow{K_2}$ (1,6) + $H_2O$
6. (1,7) + CX $\xrightarrow{K_1}$ (1,1) + $H_2O$
   $\xrightarrow{K_3}$ (1,8) + $H_2O$
   $\xrightarrow{K_4}$ (1,2) + $H_2O$
7. (1,8) + CX $\xrightarrow{K_1}$ (1,4) + $H_2O$
   $\xrightarrow{K_4}$ (1,5) + $H_2O$
8. (1,9) + CX $\xrightarrow{K_1}$ (1,2) + $H_2O$
   $\xrightarrow{K_4}$ (1,3) + $H_2O$
9. (1.10) + CX $\xrightarrow{2K_1}$ (1,7) + $H_2O$
   $\xrightarrow{2K_4}$ (1,9) + $H_2O$
10. (2,1) + CX $\xrightarrow{K_2}$ (2,6) + $H_2O$
    $\xrightarrow{K_3}$ (2,3) + $H_2O$

11. (2,2) + CX $\xrightarrow{K_2}$ (2,3) + $H_2O$

$\xrightarrow{K_2}$ (2,5) + $H_2O$

12. (2,3) + CX $\xrightarrow{K_2}$ (2,4) + $H_2O$

13. (2,5) + CX $\xrightarrow{K_2}$ (2,4) + $H_2O$

14. (2,6) + CX $\xrightarrow{K_3}$ (2,4) + $H_2O$

15. (2,7) + CX $\xrightarrow{K_1}$ (2,1) + $H_2O$

$\xrightarrow{K_4}$ (2,2) + $H_2O$

$\xrightarrow{K_2}$ (2,8) + $H_2O$

16. (2,8) + CX $\xrightarrow{K_1}$ (2,6) + $H_2O$

$\xrightarrow{K_4}$ (2,5) + $H_2O$

17. (2,9) + CX $\xrightarrow{K_4}$ (2,1) + $H_2O$

$\xrightarrow{K_3}$ (2,11) + $H_2O$

18. (2,10) + CX $\xrightarrow{2K_1}$ (2,2) + $H_2O$

$\xrightarrow{K_2}$ (2,11) + $H_2O$

19. (2,11) + CX $\xrightarrow{2K_1}$ (2,3) + $H_2O$

20. (2,12) + CX $\xrightarrow{2K_1}$ (2,7) + $H_2O$

$\xrightarrow{K_1}$ (2,9) + $H_2O$

$\xrightarrow{K_4}$ (2,10) + $H_2O$

21. $(3,1) + CX \xrightarrow{2K_1} (3,2) + H_2O$

22. $(3,2) + CX \xrightarrow{K_1} (3,3) + H_2O$

23. $(3,4) + CX \xrightarrow{2K_1} (3,1) + H_2O$

$\xrightarrow{K_1} (3,5) + H_2O$

24. $(3,5) + CX \xrightarrow{2K_1} (3,2) + H_2O$

25. $(3,6) + CX \xrightarrow{4K_1} (3,4) + H_2O$

## TABLE 5.5

### Reverse Rxns in Interconversions

1. (1,1) + $H_2O$ $\xrightarrow{2K_5}$ (1,7)
2. (1,2) + $H_2O$ $\xrightarrow{K_5}$ (1,9)
3. $\xrightarrow{K_5}$ (1,7)
3. (1,3) + $H_2O$ $\xrightarrow{K_5}$ (1,9)
4. (1,4) + $H_2O$ $\xrightarrow{K_5}$ (1,2)
   $\xrightarrow{K_5}$ (1,1)
   $\xrightarrow{K_5}$ (1,8)
5. (1,5) + $H_2O$ $\xrightarrow{K_5}$ (1,3)
   $\xrightarrow{K_5}$ (1,2)
   $\xrightarrow{K_5}$ (1,8)
6. (1,6) + $H_2O$ $\xrightarrow{K_5}$ (1,4)
   $\xrightarrow{2K_5}$ (1,5)
7. (1,7) + $H_2O$ $\xrightarrow{K_5}$ (1,10)
8. (1,8) + $H_2O$ $\xrightarrow{K_5}$ (1,9)
   $\xrightarrow{K_5}$ (1,7)
9. (1,9) + $H_2O$ $\xrightarrow{K_5}$ (1,10)

10. (2,1) + $H_2O$ $\xrightarrow{K_5}$ (1,10)

$\xrightarrow{K_5}$ (2,7)

11. (2,2) + $H_2O$ $\xrightarrow{K_5}$ (2,10)

$\xrightarrow{K_5}$ (2,7)

12. (2,3) + $H_2O$ $\xrightarrow{K_5}$ (2,2)

$\xrightarrow{K_5}$ (2,1)

$\xrightarrow{K_5}$ (2,11)

13. (2,4) + $H_2O$ $\xrightarrow{K_5}$ (2,5)

$\xrightarrow{K_5}$ (2,6)

$\xrightarrow{2K_5}$ (2,2)

14. (2,5) + $H_2O$ $\xrightarrow{K_5}$ (2,8)

$\xrightarrow{2K_5}$ (2,2)

15. (2,6) + $H_2O$ $\xrightarrow{K_5}$ (2,8)

$\xrightarrow{2K_5}$ (2,1)

16. (2,7) + $H_2O$ $\xrightarrow{K_5}$ (2,12)

17. (2,8) + $H_2O$ $\xrightarrow{K_5}$ (2,9)

18. (2,10) + $H_2O$ $\xrightarrow{K_5}$ (2,12)

19. (2,11) + $H_2O$ $\xrightarrow{K_5}$ (2,9)

$\xrightarrow{K_5}$ (2,10)

20. (3,1) + $H_2O$ $\xrightarrow{2K_5}$ (3,4)

21. (3,2) + $H_2O$ $\xrightarrow{K_5}$ (3,5)

$\xrightarrow{2K_5}$ (3,1)

22. (3,3) + $H_2O$ $\xrightarrow{4K_5}$ (3,2)

23. (3,4) + $H_2O$ $\xrightarrow{K_5}$ (3,6)

24. (3,5) + $H_2O$ $\xrightarrow{2K_5}$ (3,5)

# CHAPTER 6

## CONCLUSIONS

A kinetic model for irreversible Novolac type phenol formaldehyde polymerization has been presented and equations governing the molecular weight distribution for batch as well as homogeneous continuous - flow reactors have been derived. The set of non-linear differential equations for batch reactor are solved by Runge-Kutta method of order 4. Brown's algorithm is used to solve the set of non-linear algebraic equations derived for HCSTRs. This is found to be more efficient than the Newton's technique of solving non linear algebraic equations. The MWD thus obtained for batch reactors and HCSTRs as a function of time are presented.

R1, R2, R3 and $[P]_o / [F]_o$ are four parameters, whose effect upon the MWD of the polymer have been examined. The MWD were found to be relatively insensitive to parameters R1 and R2 and were extremely sensitive to R3. For a given R3, the distributions of $P_i$ as well as $Q_i$ fall monotonically and the conversion of phenol in HCSTRs is smaller and $Q_{1T}$ (= $Q_1 + Q_1'$) larger than those for batch reactors. For a given residence time, the number average molecular weight, $\bar{M}_n$, for HCSTR is lower but but the polydispersity index, $f$, is larger. The variation of R3 has less pronounced effect upon the MWD from HCSTR than that from the batch reactors.

The kinetic model derived for the irreversible polymerization, is extended for the reversible case.

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